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14. ABSTRACT

This technical guidance document provides site remediation managers, technical support staff, and the regulatory community with information on how to 1) assess natural attenuation processes and 2) incorporate the results of this assessment into remedy planning and implementation efforts. This document serves as an addendum to the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Air Force Center for Environmental Excellence [AFCEE], 1995). The original protocol (AFCEE, 1995) is to be retained, with this addendum serving to complement the original protocol by providing expanded guidance on developing and implementing expedited closure plans and formal exit strategies for fuel-release sites.

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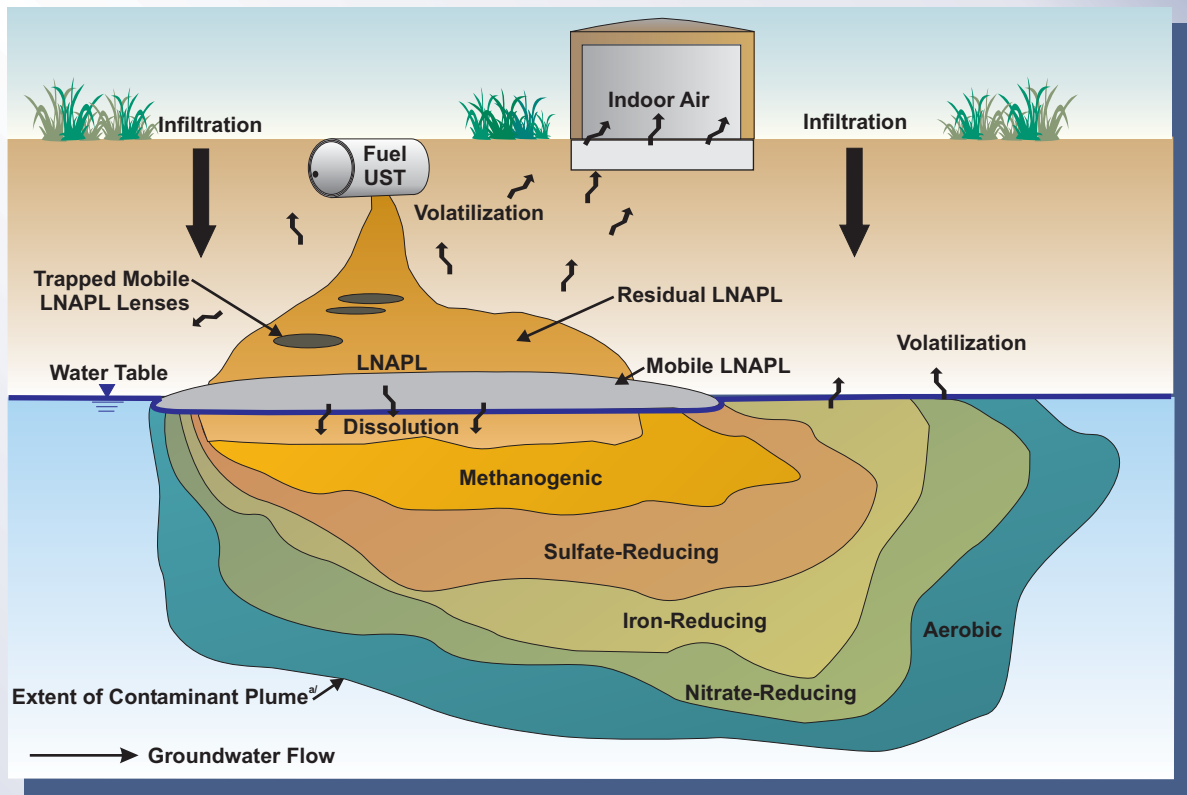
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August 2004

IMPLEMENTING MONITORED NATURAL ATTENUATION AND EXPEDITING CLOSURE AT FUEL-RELEASE SITES

Prepared for

**Air Force Center for Environmental Excellence
and
Defense Logistics Agency**

CONTRACT NO. F41624-00-D-8024

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EXECUTIVE SUMMARY

This technical guidance document provides site remediation managers, technical support staff, and the regulatory community with information on how to 1) assess natural attenuation processes and 2) incorporate the results of this assessment into remedy planning and implementation efforts. This document serves as an addendum to the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Air Force Center for Environmental Excellence [AFCEE], 1995). The original protocol (AFCEE, 1995) is to be retained, with this addendum serving to complement the original protocol by providing expanded guidance on developing and implementing expedited closure plans and formal exit strategies for fuel-release sites.

Since publication of the original protocol, significant regulatory and scientific advancements have been made in the characterization, evaluation, remediation, and regulation of fuel-release sites. For example, the growing acceptance of site-specific cleanup goals and the scientific evidence supporting monitored natural attenuation- (MNA-) based remedies has led to less intrusive and more cost-effective methods for restoring and closing sites. Over the past decade, some of the more significant scientific and regulatory advances have included:

- **Accumulation of Additional Field Evidence in Support of MNA:** Multiple studies have been published that document that the vast majority of contaminant plumes from jet fuel and gasoline releases are stable or receding (e.g., Rice *et al.*, 1996, Mace *et al.*, 1997, AFCEE, 2001a).

- **Improved Understanding of the Science of Natural Attenuation:** Research has demonstrated that biodegradation of benzene, toluene, ethylbenzene, and xlyene isomers (BTEX) and many polycyclic aromatic hydrocarbons (PAHs) occurs over a wide range of electron acceptor conditions. As described by AFCEE (1999a), sulfate reduction, methanogenesis, and iron reduction (in that order) were identified as the dominant degradation processes in BTEX plumes. In this same study, aerobic degradation was estimated to account for less than 8 percent of the total degradation at fuel sites.

- **Evaluation of Source Weathering and Active Source Reduction Measures:** The results of an AFCEE review of sites where bioventing and soil vapor extraction (SVE) were applied to source areas showed that BTEX concentrations in ground water at sites where mobile light non-aqueous phase liquid (LNAPL) has migrated into the saturated zone are often controlled by residual fuel trapped in the saturated zone during one or more seasons of the year (AFCEE, 2000a). Field observations from numerous sites have shown that natural weathering of BTEX from LNAPL often occurs at a rate that is relatively rapid and comparable to even the most aggressive LNAPL extraction processes (e.g., bioslurping, bioventing, SVE; Parsons, 2003). Based on this information, BTEX weathering from an LNAPL source in the saturated zone should be evaluated prior to prior to instituting other source reduction techniques. Only in cases where the required remediation time frame is immediate (e.g., meeting a specific clean-up standard within one year to facilitate property transfer) should complete LNAPL source removal from below the water table be considered. In these limited cases, excavation or thermal treatment will be the most effective approaches for complete source removal. Rarely can the cost of installing and operating LNAPL extraction equipment be justified because the performance of extraction technologies does not significantly accelerate BTEX dissolution relative to the rate that occurs during natural LNAPL weathering.

- **Modeling Developments:** Significant advances have been made in developing or revising user interfaces and tools that support MNA evaluations through data visualization, parameter estimation, modeling of contaminant plume migration, and modeling of LNAPL weathering.

- **Regulatory and Policy Developments:** Regulation of most underground storage tank (UST) sites has been delegated to state regulatory agencies, and a Risk-Based Corrective Action (RBCA) philosophy has become a cornerstone of most state UST regulations. Many states are currently in the process of simplifying state closure standards for fuel-release sites, as described in Section 2 of this protocol addendum.

The information provided in this protocol addendum contributes to the remedy planning process by providing 1) technical guidance on how to reach site closure using remedial strategies that account for natural attenuation and 2) updated information on advances in the evaluation and implementation of MNA-based remedies since publication of the original protocol. Following the introductory remarks in Section 1 of this addendum, information is presented on the following topics:

- *Implementing Natural Attenuation (Section 2)* is a new section that discusses the role of natural attenuation in implementing phased site restoration strategies, with a focused discussion on methods of appropriately using MNA data to achieve site closure or minimize long-term monitoring (LTM).

- *Recommended Protocol for Site Characterization (Section 3)* complements the description of site characterization techniques for supporting MNA evaluations at fuel-contaminated sites in the original protocol by providing information on more recent developments in site investigation technologies and methodologies (including LNAPL characterization). This section also discusses of the role of data quality objectives (DQOs) in scoping site characterization activities.

- *Recommended Methods for Describing and Evaluating MNA Data (Section 4)* supplements the quantitative and qualitative data presentation and analysis techniques presented in the original protocol by describing additional methods that have been shown to be useful for evaluating and demonstrating the effectiveness of MNA processes.

- *Recommended Methods for Designing and Optimizing Monitoring Networks (Section 5)* provides guidance on how LTM programs at sites where extensive monitoring networks are present can be optimized to eliminate unnecessary sampling and analysis.

Site remediation managers are encouraged to use the information provided in this protocol addendum to support development and implementation of strategic closure plans that address issues such as when to terminate source treatment and how to reduce, and eventually terminate, LTM requirements. The procedures described in this protocol addendum will aid the user in determining whether naturally-occurring degradation processes will reduce the concentrations of fuel-related contaminants of concern (COCs) to below regulatory standards before potential receptor exposure pathways are completed.

This document is not intended to prescribe a course of action that could be used in support of all possible remedial technologies. Furthermore, this document is not intended to replace or otherwise alter existing USEPA or state guidance on conducting remedial investigations (RIs) or feasibility studies (FSs). Instead, this protocol is a tool, similar to AFCEE's bioventing (Hinchee *et al.*, 1992), bioslurping (Battelle, 1995), and original MNA at fuel-release site (AFCEE, 1995) protocols, that provides guidance to practitioners on how to adequately evaluate MNA-based alternatives as part of the technology evaluation and implementation process. While this protocol

is not intended to support MNA evaluations of chlorinated solvent plumes, plumes that are mixtures of fuels and solvents, or ground water containing inorganic COCs (e.g., metals), the basic concepts presented in developing site-specific closure plans and exit strategies are applicable to a wide variety of contaminant types. In the event that chlorinated solvents or inorganic compounds are co-mingled with a fuel release, the reader is directed to two other existing protocols – *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (United States Environmental Protection Agency [USEPA], 1998a) and *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites* (Sandia National Laboratory, 1999), respectively, for further information and guidance.

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LIST OF ACRONYMS AND ABBREVIATIONS

°C	degrees centigrade
1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
λ	biodegradation rate constant
μg/L	micrograms per liter
ACGIH	American Conference of Governmental Industrial Hygienists
AEHS	Association for Environmental Health and Sciences
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
AFCEE/ERS	Air Force Center for Environmental Excellence/Science and Engineering Division
AFRPA	Air Force Real Property Agency
AMIBA	Aqueous and Mineral Intrinsic Bioremediation Assessment
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	benzene, toluene, ethylbenzene, and xylenes
BX	Base Exchange
CAA	Clean Air Act
$CaCO_3$	calcium carbonate
CCL	contaminant candidate list
CERFA	Community Environmental Response Facilitation Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm	centimeter
CMW	contingency monitoring well
CO_2	carbon dioxide
COC	contaminant of concern
COPC	contaminant of potential concern
CPT	cone penetrometer testing
CSM	conceptual site model
CWS	community water supplies
DHHS	Department of Health and Human Services
DLA	Defense Logistics Agency
DO	dissolved oxygen
DoD	United States Department of Defense
DOE	United States Department of Energy
DPT	direct-push techniques
DQO	data quality objective
DRO	diesel-range organics
EDB	ethylene dibromide
EDC	ethylene dichloride

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LIST OF ACRONYMS AND ABBREVIATIONS (Continued)

EPH	extractable petroleum hydrocarbons
ePTFE	expanded polytetrafluorethylene
ESRI	Environmental Systems Research Institute
FID	flame ionization detector
FS	feasibility study
ft/yr	feet per year
GC	gas chromatography
GMS	Groundwater Modeling System
g/mol	grams per mole
GRO	gasoline-range organics
gpm	gallons per minute
GTS	Geostatistical Temporal/Spatial
H	Henry's Law constant
HPLC	high-pressure liquid chromatography
HAS	hollow-stem auger
IARC	International Agency for Research on Cancer
IDW	investigation-derived waste
ITRC	Interstate Technology Regulatory Council
k	bulk attenuation rate constant
K_{oc}	organic carbon/water partition coefficient
K_d	soil partition coefficient
K_{ow}	octanol/water partition coefficient
k_{point}	rate constant at single point
kg	kilograms
LIF	laser-induced fluorometry
LLNL	Lawrence Livermore National Laboratory
LNAPL	light non-aqueous phase liquid
LTM	long-term monitoring
LUFT	leaking underground fuel tank
MAROS	Monitoring and Remediation Optimization System
MCL	maximum contaminant level
MDL	method detection limit
mg	milligram
mg/L	milligrams per liter
MIP	Membrane Interface Probe
MK	Mann-Kendall
MNA	monitored natural attenuation
MNO	monitoring network optimization
MtBE	methyl tert-butyl ether
mV	millivolts
NAC	natural attenuation capacity
NAS	Natural Attenuation Software
NFA	No Further Action

NPDWR	National Primary Drinking Water Regulation
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory
NTU	nephelometric turbidity unit
OPS	Operating Properly and Successfully
ORP	oxidation-reduction potential
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbon
PCBs	polychlorinated biphenyls
PDBS	passive diffusion bag samplers
PID	photoionization detector
PMW	performance monitoring well
PLFA	phospholipid fatty acids
QA	quality assurance
QC	quality control
RBCA	Risk-Based Corrective Action
RCRA	Resource Conservation and Recovery Act
redox	reduction/oxidation
RFG	reformulated gasoline
RI	remedial investigation
RPM	restoration project manager
RPO	remedial process optimization
ROST	Rapid Optical Screening Tool
SAP	Sampling and Analysis Plan
SCAPS	Site Characterization and Analysis Penetrometer System
SFDT	sampling frequency decision trees
SMCL	secondary maximum contaminant level
SVE	soil vapor extraction
SVOC	semi-volatile organic compound
SWRCB	State of California Water Resources Control Board
TAL	target analyte list
TAME	tert-amyl methyl ether
TBA	tert-butyl alcohol
TEAP	terminal electron accepting process
TEH	total extractable hydrocarbons
TeMB	tetramethylbenzene
TEPH	total extractable petroleum hydrocarbon
TMB	trimethylbenzene
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TRPH	total recoverable petroleum hydrocarbons
TVH	total volatile hydrocarbons
UC	University of California

LIST OF ACRONYMS AND ABBREVIATIONS (Concluded)

USAF	United States Air Force
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	underground storage tank
VFA	volatile fatty acids
VOC	volatile organic compound
VPH	volatile petroleum hydrocarbons
Y_m	yield coefficient

SECTION 1

INTRODUCTION

This technical guidance document is intended to provide restoration project managers (RPMs), technical support staff, and the regulatory community with information on how to assess natural attenuation processes and incorporate the results of this assessment into remedy planning and implementation efforts. This document serves as a supplement to the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Air Force Center for Environmental Excellence [AFCEE], 1995). The original protocol (AFCEE, 1995) is to be retained and is referred to throughout this document. This document provides information that complements the original protocol by providing expanded guidance on developing and implementing expedited closure plans and formal exit strategies for fuel-release sites.

The information presented in the original protocol (AFCEE, 1995) was prepared through the joint effort of AFCEE's Science and Engineering Division (AFCEE/ERS) (formerly the Technology Transfer Division); the Bioremediation Research Team at the United States Environmental Protection Agency (USEPA) National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma, and Parsons. The purpose of the original protocol was to facilitate implementation of monitored natural attenuation (MNA) at fuel-hydrocarbon-contaminated sites owned by the United States Air Force (USAF), other United States Department of Defense (DoD) agencies, and public interests. This addendum, developed jointly by AFCEE/ERS, the Defense Logistics Agency (DLA), and Parsons, provides new and/or expanded discussion on relevant topics, as described in Section 1.3.

1.1   BENEFITS AND LIMITATIONS OF MONITORED NATURAL ATTENUATION

The *AFCEE Remediation Matrix - Hierarchy of Preferred Alternatives* (AFCEE, 1994) identifies MNA as the first option to be evaluated at USAF sites. This matrix implies only that MNA should be evaluated prior to proceeding (if necessary) to more costly solutions (e.g., pump and treat), and is not intended to imply the presumptive selection of MNA in every case. This recommendation is consistent with recent USEPA guidance documents on MNA (e.g., the Office of Solid Waste and Emergency Response [OSWER] directive on the *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* [USEPA, 1999a]) that indicate that USEPA does not currently consider MNA a presumptive remedy, but rather as one alternative that should be compared to other applicable remedies for a given site.

There are several potential benefits of implementing MNA as part of a site remedy, including:

- Fuel-related contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide and water) through biodegradation, rather than distributed to another phase or location within the environment;

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- MNA is non-intrusive and allows continuing use of site infrastructure during subsurface remediation;

- Implementation of an MNA alternative may pose less risk to potential receptors than some active site remediation activities because the MNA alternative does not actively produce new exposure pathways due to disturbance of contaminated media;

- MNA typically is less costly than other available active remedial technologies (e.g., pump and treat);

- MNA is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime); and

- Many of the fuel-related compounds that are the most mobile and toxic (e.g., benzene, toluene, ethylbenzene, and xylenes [BTEX]) are also the most susceptible to biodegradation (with the notable exception of the gasoline oxygenate methyl-tertiary-butyl ether [MtBE]).

Potential limitations on the effectiveness or appropriateness of MNA may include:

- Naturally-occurring and/or institutionally-induced changes in local hydrogeologic conditions have the potential to cause changes in ground-water flow direction and velocity, pH, electron acceptor concentrations, or the rate at which contaminant mass enters the ground-water system, all of which may adversely affect MNA processes;

- As with any *in situ* remedial technology, aquifer heterogeneity may complicate or otherwise limit development of an accurate conceptual site model (CSM) that can be used as the basis for evaluating the MNA alternative;

- Time frames for achieving site closure may be longer than more active remedial alternatives, resulting in time delays that are not acceptable in terms of intended future land use and/or property transfer;

- Institutional controls may be necessary to ensure long-term protectiveness; and

- More extensive education and outreach efforts may be required to gain public and/or regulatory acceptance of MNA.

1.2   DOCUMENTING THE OCCURRENCE OF NATURAL ATTENUATION

To support implementation of MNA as a site remediation strategy, a property owner must scientifically demonstrate that degradation of site contaminants of concern (COCs) is occurring at rates sufficient to be protective of human health and the environment. Since the publication of the original fuels protocol document (AFCEE, 1995), regulatory guidance from USEPA has been formalized, primarily through the aforementioned OSWER directive (USEPA, 1999a). USEPA guidance clearly indicates that up to three lines of evidence may be required to support implementation of MNA as a remedial measure. As indicated in the OSWER directive, these lines of evidence are:

1. Documentation of historical decreases in contaminant mass and/or concentration at the field scale over time;

2. Hydrogeologic and geochemical data that indirectly demonstrate the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to the required level; and

3. Data from field or microcosm studies that provides direct microbiological evidence that the COCs are being degraded at the site.

The first, or primary, line of evidence involves using statistically significant historical trends in contaminant concentration in conjunction with aquifer hydrogeologic parameters, such as ground-water velocity, diffusion, and dispersion, to show that a reduction in the total mass of contaminants is occurring at the site. The second line of evidence is used to provide an indication of the natural attenuation mechanism(s) that are acting to stabilize and/or decrease the size of the contaminant plume. Support for this second line of evidence involves the collection and interpretation of geochemical indicator parameter data that can be used to identify active metabolic processes. Use of the third line of evidence, direct microbiological study, should be implemented only when the interpretation from the first two lines of evidence is insufficient or inconclusive in demonstrating on-going *in situ* biodegradation of fuel-related contamination. In addition to these three lines of evidence described in the OSWER directive on MNA, the *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Sites* (American Society of Testing and Materials [ASTM, 1998a]) indicates that additional activities, such as solute transport modeling and/or estimates of assimilative capacity, may be useful as an optional third line of evidence for the analysis of data collected as part of evaluating the primary and secondary lines of evidence.

1.3   PURPOSE AND SCOPE OF PROTOCOL ADDENDUM

The purpose of this document is to provide technical guidance on developing and implementing site closure strategies while also supplementing the description of methods for evaluating and supporting an MNA alternative at fuel-release sites that was originally presented in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (AFCEE, 1995). The original protocol (AFCEE, 1995) is to be retained, and is referred to throughout this document. The current document provides information on pertinent topics that either were not included or were discussed in a limited fashion in the original protocol. Specific topics covered in this addendum are summarized below:

- A new section has been added to discuss the role of natural attenuation in implementing phased site restoration strategies, with a focused discussion on methods of appropriately using MNA data to achieve site closure or minimize long-term monitoring (LTM). Included in this section is a discussion of the current status of state regulations and guidance regarding documentation and use of MNA as a remedial alternative at fuel-release sites;

- The description of site characterization techniques that can be used in support of MNA evaluations at fuel-release sites has been supplemented to include information on more recent developments in site investigation technologies and methodologies (including light non-aqueous phase liquid [LNAPL] characterization);

- Discussion of the role of data quality objectives (DQOs) in scoping site characterization activities has been added;

- The discussion of quantitative and qualitative data presentation and analysis techniques has been expanded to a separate section that includes additional methods that may be helpful in evaluating and demonstrating the effectiveness of MNA processes; and

- A new section dedicated to discussion of LTM programs and monitoring network optimization (MNO) techniques has been added, with the goal of facilitating

development of effective (in terms of both cost and performance) LTM monitoring plans that provide appropriate data to demonstrate regulatory compliance and verify MNA performance.

The information provided in the current document is an important component of the remedy planning process because it provides the technical basis for 1) selecting and implementing an MNA-based alternative and 2) reaching site closure using cost-effective remedial strategies that account for natural attenuation processes that contain and treat petroleum hydrocarbons *in situ*.

The intended audience for this document includes site RPMs, their contractors, scientists, and consultants, the regulatory community, and others charged with remediating ground-water that is contaminated with fuel hydrocarbons. RPMs are encouraged to use the information provided in this protocol addendum to help develop and implement strategic closure plans that address issues such as when to terminate source treatment and how to reduce, and eventually terminate, LTM requirements. It is intended that this protocol addendum will allow the user to determine whether naturally-occurring degradation processes will reduce the concentrations of fuel-related COCs to below regulatory standards before potential receptor exposure pathways are completed. Note that the evaluation of receptor pathways should include consideration of both existing exposure pathways and potential pathways that may arise from future use of the site. This protocol is intended to be used within the established regulatory framework, and site-specific discussions with regulatory agencies will likely be required as part of the process of achieving site-specific remedial objectives.

This document is not intended to prescribe a course of action that could be used in support of all possible remedial technologies. Instead, this protocol is a tool, similar to AFCEE's bioventing (Hinchee *et al.*, 1992) or bioslurping (Battelle, 1995) protocols, that provides guidance to practitioners on how to adequately evaluate these alternatives in subsequent feasibility studies (FSs) or other technology evaluations. Furthermore, this protocol is not intended to support MNA of chlorinated solvent plumes, plumes that are mixtures of fuels and solvents, or ground water containing inorganic COCs (e.g., metals). In the event that chlorinated solvents or inorganic compounds are found to be co-mingled with a fuel release, the reader is directed to two other existing protocols – *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (USEPA, 1998a) and *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites* (Sandia National Laboratory, 1999), respectively – as sources of further information and guidance. Finally, this document does not replace or otherwise alter existing USEPA or state guidance on conducting remedial investigations (RIs) or FS evaluations.

1.4   COMMON CONTAMINANTS OF CONCERN AT FUEL-RELEASE SITES

COCs are defined as those chemicals that pose a risk to human health or the environment. Although COCs may vary between fuel-release sites, the most common COCs at fuel-release sites are BTEX, polycyclic aromatic hydrocarbons (PAHs; also referred to as polyaromatic hydrocarbons or polynuclear aromatic hydrocarbons), and fuel additives (e.g., MtBE and lead). BTEX compounds are the primary volatile constituents of petroleum-distillate fuels, and are commonly identified as COCs at fuel-contaminated sites because they are relatively toxic and are more mobile than most other fuel constituents when released into the environment. PAHs [e.g., naphthalene, pyrene, benzo(a)pyrene] are semi-volatile organic compounds (SVOCs) that generally pose toxicity and carcinogenic concerns for human health and the environment. PAHs contain two or more benzene-ring structures, and are generally less volatile, less soluble, and more strongly sorbed than BTEX compounds. As a result of the chemical properties of PAHs,

these compounds are less mobile than aromatic hydrocarbons in the environment. Fuel additives are generally added to gasoline as anti-knocking agents and to reduce carbon monoxide and ozone emissions. For example, addition of oxygenates to create reformulated gasoline has been one method of improving air quality in localities that do not meet the National Ambient Air Quality Standards, as required by the Clean Air Act (CAA). Currently, the oxygenates MtBE and ethanol are the most common fuel additives used to meet the oxygen content requirements for reformulated gasoline specified in the CAA. Historically, other additives (e.g., tetraethyl lead) have been added to gasoline to prevent knocking during combustion. The toxicity of gasoline additives varies by compound. For example, the use of tetraethyl lead as an anti-knock agent for highway vehicles was banned as of January 1, 1996 due to health concerns over the toxicity of this compound. For MtBE, recent investigations suggest that the acute toxicity of this compound in exposed animals and humans is low, but the potential human risk of developing cancer from long-term exposure to MtBE and/or its metabolites is unknown and currently under investigation (USEPA, 1997a). Due to these toxicity concerns, and the observed presence of MtBE in private and public drinking water supplies, several states are currently proposing legislation that would ban the use of MtBE in gasoline. In advance of a potential ban on the use of MtBE as a fuel oxygenate, and as a mitigation effort for the potential release of MtBE into the environment, there has been an increase in the use of ethanol as a fuel oxygenate in recent years, as ethanol is considered non-carcinogenic. Appendix A provides additional detail on the physical and chemical properties of the most common COCs at fuel-release sites.

Federal maximum contaminant levels (MCLs) have been established for several common fuel constituents, as listed below in **Table 1-1**. Although MCLs are specifically applicable to drinking water, these standards are often used as *in situ* target concentrations for remediation in drinking water aquifers. Two other compounds that may be found at fuel-release sites (MtBE and naphthalene) are listed on the federal contaminant candidate list (CCL). Note that constituents on the CCL are not currently subject to any proposed or promulgated national primary drinking water regulation (NPDWR); compounds are listed on the CCL because they are either known or anticipated to occur in public water systems, and because there is concern that these compounds may require regulation under the Safe Drinking Water Act. For MtBE, USEPA is considering the establishment of a secondary maximum contaminant level (SMCL), based on aesthetic concerns of taste and odor. In advance of promulgating a standard for MtBE concentrations, USEPA (1997a) has issued a drinking water advisory that recommends that MtBE concentrations not exceed 20 micrograms per liter (µg/L) to 40 µg/L to protect consumer acceptance of water quality (based on taste and odor concerns) and to provide a "large" margin of exposure safety from toxic effects.

TABLE 1.1
FEDERAL MAXIMUM CONTAMINANT LEVELS FOR SELECTED FUEL COMPONENTS

Compound	MCL (µg/L)
Benzene	5
Toluene	1,000
Ethylbenzene	700
Xylenes (Total)	10,000
Benzo(a)pyrene	0.2

Source: USEPA, 2003a

Since publication of the original technical protocol on MNA at fuel-release sites (AFCEE, 1995), regulatory oversight of most fuel-release sites that do not have other COCs (e.g., chlorinated solvents, metals) has continued to be delegated to the state agency that is responsible for the underground storage tank (UST) program. Many of these state programs have standards that apply to either individual fuel compounds (e.g., naphthalene) or to groups of compounds (e.g., gasoline-range organics [GRO] and diesel-range organics [DRO]) that are not regulated by federal MCLs. In addition, some states (e.g., California, Massachusetts) have established primary (i.e., health-based) or secondary (i.e., aesthetic) standards for MtBE in drinking water in advance of federal establishment of an MCL for this compound. The reader is directed to Appendix B for a summary of state perspectives on use of MNA at fuel-release sites, a list of state-specific regulated compounds (as of Spring 2003), and a list of state agencies that are currently responsible for fuel-release sites.

In addition to COCs that are constituents of the actual fuel release, the reduced geochemical condition that typically develops in the subsurface environment following the introduction of an anthropogenic carbon source (e.g., fuel) has the potential to chemically transform naturally-occurring metallic (e.g., manganese, iron) or related non-metallic (e.g., arsenic) elements into aqueous species that are more mobile and sometimes more toxic than the original solid-phase species that were present when the aquifer was pristine. Although the comprehensive risk assessment process is not specifically described as part of this protocol, sampling and analysis for metals or related nonmetallic elements that have applicable primary (e.g., arsenic) or secondary (e.g., manganese, iron) standards may be required to comply with applicable federal or state regulations. It is important to note that arsenic, iron, manganese and other species that can be mobilized by reducing conditions will rapidly precipitate back out of solution when they reach downgradient areas that are naturally oxidizing.

1.5   ADVANCES IN OUR UNDERSTANDING OF NATURAL ATTENUATION

Since 1992, the USAF has implemented MNA at hundreds of fuel-release sites across the United States and abroad. Both the science supporting MNA, and the regulatory policy to implement MNA, have evolved over the past decade. The following subsections provide a summary of some of the more significant advances in recent years, and how these advances have been incorporated into this protocol addendum.

Additional Field Evidence Supporting MNA

- Statistical studies conducted in California and Texas in the mid 1990s, using data from nearly 2,000 petroleum sites, concluded that between 80 and 90 percent of benzene plumes are stable or receding, and are less than 260 feet long. Less than 3 percent of these sites posed any risk to drinking water supplies or human or ecological receptors. Section 2.1.1 provides additional description of the data and findings of these studies.

- From 1992 to 1998, AFCEE completed an initial evaluation of 42 jet fuel- and gasoline-contaminated sites and found that 87 percent of the sites had stable or receding plumes. Five years later, AFCEE returned to seven of these sites to determine if model-predicted BTEX reductions were accurate. This study found that, although monitoring wells located at the source of the spill had more-persistent BTEX levels, BTEX concentrations in monitoring wells in the downgradient portion of the plume showed significant reductions over time due to biodegradation (AFCEE, 2001a).

Improved Understanding of the Science of Natural Attenuation

- Research has demonstrated that biodegradation of BTEX (and many PAHs) can and does occur over a wide range of electron acceptor conditions. The results of this research have been summarized by others, including Suarez and Rifai (1999), who provide a compendium of reported degradation rates for various contaminants that are commonly found at fuel-release sites.

- Based on AFCEE MNA studies, aerobic degradation was estimated to account for less than 8 percent of the total degradation at fuel sites. As described in AFCEE (1999a), sulfate reduction, methanogenesis, and iron reduction (in that order) were identified as the dominant degradation processes in BTEX plumes.

- The AFCEE-led draft Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) protocol was developed to provide a more accurate estimate of the total mass of electron acceptors in the aquifer matrix that is available for biodegradation of petroleum hydrocarbons. Application of the AMIBA protocol has suggested that previous estimation methods (based solely on dissolved ferrous iron concentrations) significantly under-predict iron-based biodegradation of petroleum hydrocarbons, and that iron-reduction is (by far) the dominant attenuation process for at least some of the sites studied under the AMIBA program (AFCEE, 2000b).

Importance of Source Reduction

- The AFCEE bioslurping initiative demonstrated that bioslurping could be used to increase short-term LNAPL recovery rates. This same initiative also confirmed previous field observations that it is inherently difficult to remove mobile LNAPL (i.e., free product) with extraction methods. Information on this initiative is provided at the following location on the AFCEE web site:
  http://www.afcee.brooks.af.mil/products/techtrans/bioslurping.asp.

- An AFCEE (2000a) review of 12 bioventing and soil vapor extraction (SVE) sites showed that BTEX concentrations in ground water are controlled by fuel trapped in the saturated zone during one or more seasons of the year. Unless these saturated zone residuals are addressed through more aggressive remedial methods (e.g., biosparging, chemical oxidation, excavation), dissolved BTEX will continue to persist in the source area. Note that this study did show that bioventing and SVE can be very effective remedial approaches for removal of BTEX from soil and soil gas in the unsaturated zone.

- Parsons (2003) recently completed an AFCEE-funded update study of LNAPL weathering to determine how rapidly BTEX compounds are naturally removed from LNAPL. The study concluded that observed source decay rates could be approximated by a first-order decay rate. As an example, the average weathering rate for benzene was estimated as 19 percent per year for the sites evaluated as part of this study. LNAPL at sites with sandy soils and higher ground-water velocities was observed to weather at faster rates than was observed at sites with silt and clay soils and lower ground-water velocities.

- If the desired remediation time frame is short (e.g., achieve clean-up within one year to facilitate property transfer), complete source removal will be required if residual LNAPL is present. The results of the above initiatives demonstrate that complete LNAPL removal from the saturated zone can only be accomplished by excavation or

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thermal treatment, as even the most aggressive extraction technologies (e.g., bioslurping, bioventing, SVE) rarely remove more than 50 percent of the residual LNAPL. Thermal heating is an expensive option that makes sense only if the LNAPL source is small and at a depth where excavation is prohibitively difficult or expensive.

- At sites where the acceptable remediation time frame is longer (e.g., remediation can be allowed to occur over years or decades at an active installation) or source excavation is not possible, natural weathering of the LNAPL source is an effective and appropriate process for reducing BTEX dissolution to ground water. In terms of achieving site remediation goals for ground water, use of engineered extraction technologies has not been shown to provide long-term benefits that are significantly different from what occurs during natural weathering of BTEX from the LNAPL source.

Modeling Developments

- Analytical models, such as the AFCEE-developed BIOSCREEN (USEPA, 1996a; Groundwater Services, Inc. [GSI], 1997), Natural Attenuation Software (Chapelle *et al*., 2003), and BioTrends (http://www.waterloohydrogeologic.com), have either been developed or updated and revised to aid in interpreting natural attenuation data by incorporating methods for estimating source decay rates, natural attenuation rates of dissolved contaminants, and/or remediation time frames.

- Visualization tools have been integrated with data management systems to provide graphical representations of spatial and temporal variation in reduction/oxidation (redox) condition (e.g., SEQUENCE [Carey *et al*., 2003])

- Numerical models of reactive contaminant fate and transport, such as the AFCEE developed BIOPLUME III (USEPA, 1998b) and SEAM3D (Waddill and Widdowson, 1998), have been refined to explicitly simulate the effects of petroleum hydrocarbon biodegradation via sequential electron acceptor processes for biodegradation.

- To assist site managers in simulating and predicting site-specific free- and residual-product weathering of BTEX compounds, AFCEE developed a model (SourceDK™) for source decay estimation (GSI, 2004).

Cost of MNA Implementation

- Costs of implementing MNA have steadily decreased as the emphasis has shifted from extensive geochemical analysis and modeling to greater reliance on historical data and optimized monitoring. Current costs for evaluating MNA and preparing a risk-based site closure plan range from approximately $40,000 to $60,000 per site.

- Based on a review of AFCEE demonstration sites, an average of 11 LTM wells is recommended for tracking the progress of MNA. The average timeframe to achieve MCLs at these sites was predicted to be 22 years (AFCEE, 1999a).

- MNA costs can be reduced by optimizing the LTM well network and limiting the sampling frequency and target analyte list ([TAL]; AFCEE, 2000c). As discussed in Section 5, tools such as Monitoring and Remediation Optimization System (MAROS) (AFCEE, 2002; Aziz *et al*., 2002) and other qualitative and statistical methodologies are available to systematically optimize LTM networks.

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Regulatory and Policy Developments

- ASTM (1995a) published a Risk-Based Corrective Action (RBCA) Standard that recommends MNA of BTEX compounds as a cornerstone of the RBCA strategy for ground water.

- Most state UST regulations now incorporate all or part of the RBCA philosophy. States are generally in the process of simplifying state closure standards for fuel-release sites by requiring the site owner to 1) manage risks posed by contaminated soil by using excavation restrictions and 2) demonstrate the efficacy of MNA for dissolved contaminants using ground-water monitoring data.

- In addition to the 1999 OSWER policy directive, USEPA has published a number of resources to assist site managers and regulatory agencies in explaining the advantages and disadvantages of MNA to the public. As described in Section 2.1, most FS evaluations include MNA as a baseline alternative.

- Other industry groups, including the American Petroleum Institute (API) and ASTM, have produced a variety of technical resources relating to fuels remediation and MNA, which are also described in Section 2.1.

1.6 DOCUMENT ORGANIZATION

This document contains six sections, including this introduction, and four appendices. Section 2 presents 1) a summary of current regulatory guidance on MNA of fuel-contaminated sites, 2) a discussion of how to develop site exit strategies, and 3) a discussion of the role of MNA at sites with various future land use plans. Section 3 presents a recommended protocol that can be used to obtain appropriate and scientifically valid data for evaluation of the MNA alternative. Section 4 describes various methods of data representation and modeling that can be used to support and demonstrate the potential effectiveness of the MNA alternative. Section 5 discusses post-modeling activities, including MNO, that are recommended as an aide to cost-effectively demonstration the long-term effectiveness of the MNA approach. Section 6 lists references used in preparing this document.

Each appendix to this document provides additional detailed supporting information. Appendix A describes 1) physical and chemical properties of the most common COCs at fuel-contaminated sites, 2) how these properties affect the fate and transport of fuel-related compounds in the subsurface environment, and 3) both destructive and nondestructive mechanisms of MNA. Appendix B provides 1) a summary of state perspectives on MNA and 2) a list of state-specific regulated compounds for contaminants that are commonly found at fuel-release sites. Appendix C describes 1) the development of a CSM for a fuel-contaminated site and 2) provides an overview of the exposure assessment process that is an important component of CSM development. Appendix D describes methods than can be used for collection of site characterization and monitoring data necessary to support MNA, including sampling procedures and analytical protocols for LNAPL characterization, quantification of soil properties, and measurement of hydrogeologic and ground-water geochemical conditions.

SECTION 2

IMPLEMENTING NATURAL ATTENUATION

The purpose of this section is to describe currently available guidance on implementation of MNA at fuel-release sites, provide a summary of the components of developing a site exit strategy, provide recommendations on methods of implementing MNA as part of the overall site exit strategy, and to describe information that will be required prior to achieving site closure and/or property transfer.

2.1   GUIDANCE FOR REMEDIATING FUEL-RELEASE SITES

Since publication of the original technical protocol on MNA at fuel-release sites (AFCEE, 1995), significant regulatory and scientific advancements have been made in the characterization, assessment, remediation, and regulation of fuel-release sites. The growing acceptance of site-specific cleanup goals and scientific evidence supporting the MNA alternative have led to less intrusive and more cost-effective methods of remediating and closing these sites. The purpose of this section is to provide an overview of some of the significant studies and regulatory documents that support the use of MNA for fuel-release sites.

2.1.1   Risk-Based Corrective Action Programs

Faced with the reality that the resources allocated for leaking UST site remediation are significantly less than what would be needed to return every leaking UST site to pristine conditions, multiple efforts performed during the mid- to late-1990s focused on how to use RBCA programs to allocate limited resources to achieve maximum benefit to society in terms of overall risk-reduction (e.g., Small, 1998). The following sections discuss several of the initiatives and studies that provided the support needed to establish the RBCA approach, and are intended to provide background information and summaries of case studies that can be used to support on-going site closure efforts.

2.1.1.1   AFCEE Initiatives

In 1992, AFCEE began two major technology demonstration programs to encourage widespread application of bioventing and natural attenuation at USAF sites. The successful demonstration of natural attenuation at over 50 sites located across the nation stimulated international interest in the use of this cost-effective method of reducing the risk associated with BTEX compounds. From 1994 to 1999, AFCEE completed multiple risk-based site closure initiatives that combined the merits of natural attenuation, low-cost source removal, and site-specific risk-based cleanup criteria to streamline the site closure process. The AFCEE website, located at http://www.afcee.brooks.af.mil/products/techtrans/treatmenttechnologies.asp, contains summaries of these projects.

2.1.1.2   ASTM RBCA Standard

In response to the realization that the resources available to fund remediation of leaking UST sites under state leaking UST programs were, or were on the verge of, being consumed prior to achieving 'pre-leak' conditions, USEPA, OSWER, and private industry (led by ASTM) collaborated to develop a risk-based decision framework that facilitated categorization and prioritization of leaking UST cleanup sites (Small, 1998). This risk-based approach to site remediation, as described in the *Standard Guide for Risk-Based Correction Action Applied at Petroleum Release Sites* (ASTM, 1995a), was developed to provide a more consistent and rational decision-making process for the remediation of petroleum-release sites, and specifically the hundreds of thousands of contaminated gasoline station sites across the United States. A three-tiered approach, as described in Section 2.3.4 of this protocol, was designed to provide the site owner and regulatory agencies with a consistent method of classifying sites as to the urgency and scope of cleanup required at each site. In addition, MNA of BTEX compounds in ground water was established as a cornerstone of the RBCA strategy. State UST regulations now incorporate most, if not all, of the RBCA philosophy outlined in the ASTM standard. It is interesting to note that, as of September 2002, USEPA (2002a) statistics indicate that the number of 'backlog' sites (i.e., sites where UST releases have been confirmed but site closure has not been reached) has fallen by 19 percent from the peak of more than 176,000 sites in 1995.

2.1.1.3   Lawrence Livermore National Laboratory Study

In June 1994, the State of California Water Resources Control Board (SWRCB) retained the Lawrence Livermore National Laboratory (LLNL) and the University of California (UC) to study the cleanup of leaking underground fuel tanks (LUFTs) in the state. The study consisted of data collection and analysis of over 1,200 LUFT case studies located in California (Rice *et al.*, 1996). The study, which focused on dissolved benzene plumes and how these plumes have migrated and decreased in concentration over time, concluded that 90 percent of the benzene plumes were less than 260 feet long and were either stable or shrinking in size. The study also concluded that 75 percent of the plumes were confined to shallow aquifers, and that a very small percentage of these sites actually posed a risk to drinking-water supplies or human or ecological receptors.

2.1.1.4   University of Texas Plume Study

In 1997, the University of Texas published a detailed statistical analysis of 605 sites with petroleum-contaminated ground water (Mace *et al*., 1997). The results fully supported the findings of the LLNL/UC study. Benzene plumes of less than 250 feet were observed at 75 percent of the sites, and only 3 percent of the plumes were determined to be increasing in length. Although 60 percent of the sites had public or private wells within a 0.5-mile radius, less than 5 percent of the plumes were posing an immediate threat to public health. Natural attenuation and/or solute transport limitations (attributed to low aquifer permeability) were determined to be the two phenomena that were effectively preventing downgradient migration of ground-water contaminant plumes at the majority of fuel-release sites in Texas.

2.1.1.5   Evolution of Regulatory Perspective

Beginning in the early 1990s, many state regulators began to realize that few petroleum release sites posed an immediate risk to human or ecological receptors, and that significant private and taxpayer money was being spent for relatively little risk-reduction benefit. Many state UST reimbursement funds were depleted with little to show in the way of health-protective remediation (Small, 1998). Today, all 50 states have adopted some type of risk-based approach

for petroleum sites. Many states are simplifying site closure standards and requiring that the site owner manage risks through preventing contact with contaminated soil by using excavation restrictions and demonstrating the effectiveness of MNA using ground-water monitoring data. The AFCEE website (http://www.afcee.brooks.af.mil/products/techtrans/riskbased.asp) includes a summary of state UST regulations, and Appendix B provides a summary of state regulatory contacts, state-specific approaches to MNA, and discussion of the types of compounds regulated.

In light of these scientific advances and state and federal regulatory agency recognition of natural attenuation and risk-based remediation, AFCEE has recommended that USAF RPMs assess the potential of the MNA alternative for all sites (including non-petroleum sites) entering the FS or remedial design phase. AFCEE has further recommended that sites with active ground-water pumping systems be reassessed to determine if MNA is a more effective long-term remediation strategy in terms of cost and performance (AFCEE, 1994).

2.1.2   USEPA Policy and Technical Guidance

Remediation activities at the majority of fuel-release sites are now regulated by state UST agencies. Relative to federal regulatory requirements, state UST regulations tend to be simpler to follow, with more streamlined reporting, remediation, and monitoring requirements. In an effort to facilitate a more consistent application of MNA, USEPA (1999a) published *Directive 9200.4.17P*, *Use of MNA at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. The directive encourages site managers and regulatory agencies to evaluate MNA as a part of the site characterization process for all sites, including fuel and chlorinated solvent sites. The directive states:

> "*Once site characterization data has been collected and a conceptual site model developed, the next step is to evaluate the efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate, with an acceptable level of confidence, both the rate of attenuation processes and the anticipated time required to achieve remediation objectives.*"

One of the purposes of this protocol is to assist the site manager in efficiently accomplishing the level of MNA evaluation required by this USEPA directive.

In addition to this policy directive, USEPA has published a number of resources to assist site managers and regulatory agencies in explaining the pros and cons of MNA to the public. Three documents on the use of MNA at contaminated sites that are accessible from the USEPA website (http://www.epa.gov/swerust1/oswermna/mna_epas.htm) include:

- *A Citizen's Guide to Natural Attenuation - EPA 542/F-01/004* (USEPA, 2001a);

- *Monitored Natural Attenuation of Petroleum Hydrocarbons - USEPA Remedial Technology Fact Sheet – EPA 600/F-98/021* (USEPA, 1999b); and

- *Commonly Asked Questions Regarding the Use of Natural Attenuation for Petroleum Contaminated Sites at Federal Facilities*, which can be accessed from the USEPA website located at http://www.epa.gov/swerffrr/documents/petrol.htm.

2.1.3   Other Sources of Guidance

In addition to AFCEE and USEPA guidance on fuels remediation and ground-water MNA, site managers are encouraged to contact their local state regulators to see if the state agencies have published specific guidance on MNA. Many states have implemented their own guidance based on modifications to the original protocol (AFCEE, 1995) and the ASTM (1995a) RBCA standard. Other industry groups, such as API and ASTM have produced a variety of technical

resources relating to fuels remediation and MNA. Two specific resources that may provide useful reference information include:

- *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites* (ASTM, 1998a); and

- *API Groundwater Protection Homepage* (Accessible from the API Environment, Safety, and Health homepage located at http://api-ep.api.org/environment/index.cfm), which includes information on special topics such as managing risk at LNAPL sites, an MtBE Resource Center, and an LNAPL Resource Center.

2.2   DEVELOPING A SITE CLOSURE STRATEGY

In an effort to reduce the cost and time of cleaning up fuel-release sites, the USAF has developed a streamlined remediation and site closure approach (AFCEE, 1998) that is comprised of three key elements:

- Development and use of site-specific cleanup standards;

- Scientific documentation of natural attenuation; and

- Cost-effective source reduction, when required.

Use of this approach will result in more achievable cleanup goals and the maximum use of natural attenuation and other cost-effective cleanup techniques, and more cost-effective site closures. **Figure 2.1** presents a logic/decision tree to guide the site closure process at fuel-release sites. The reader is encouraged to use this decision tree to determine the role of MNA in the overall site closure process.

2.2.1   Use of Site-Specific Cleanup Objectives

The majority of DoD fuel-release sites are located in industrial areas with minimal contact between contaminated media and human or ecological receptors. Based on hundreds of plume studies at fuel-release sites, it is readily observable that natural attenuation processes have already contained most plume migration and will eventually remediate petroleum-impacted ground water. With additional controls such as excavation restrictions, many small fuel-release sites can and should be placed in a "managed risk" or limited-monitoring status, without requiring engineered remediation.

RBCA guidance and most state UST regulations encourage the use of site-specific cleanup objectives that seek to establish numerical cleanup standards based on site-specific exposure pathways. Because soil and ground-water contact is limited in most industrial/airfield scenarios, cleanup requirements for soil and ground water are less stringent than in residential areas. RPMs should seek to establish remedial objectives that match the potential exposure risk at each site. For additional information on establishing site-specific and risk-based cleanup objectives, the reader should refer to the *Air Force Handbook for Remediation of Petroleum Contaminated Sites* (AFCEE, 1998) on the AFCEE website.

2.2.2   Scientific Documentation of Natural Attenuation

Site-specific strategies for ground-water contaminant remediation at fuel-release sites should be centered on the proper characterization and evaluation of natural attenuation mechanisms. Sections 3 and 4 of this protocol update describe methods of data collection and analysis that can be used to provide scientific documentation of natural attenuation at fuel-release sites. This protocol update encourages the use of MNA as the centerpiece of site closure strategy and

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FIGURE 2.1
DECISION TREE FOR ACHIEVING SITE CLOSURE/PROPERTY TRANSFER AT FUEL RELEASE SITES

NOTES

CSM = Conceptual Site Model
LTM = Long-Term Monitoring
NFA = No-Further Action
OPS = Operating Properly and Successfully
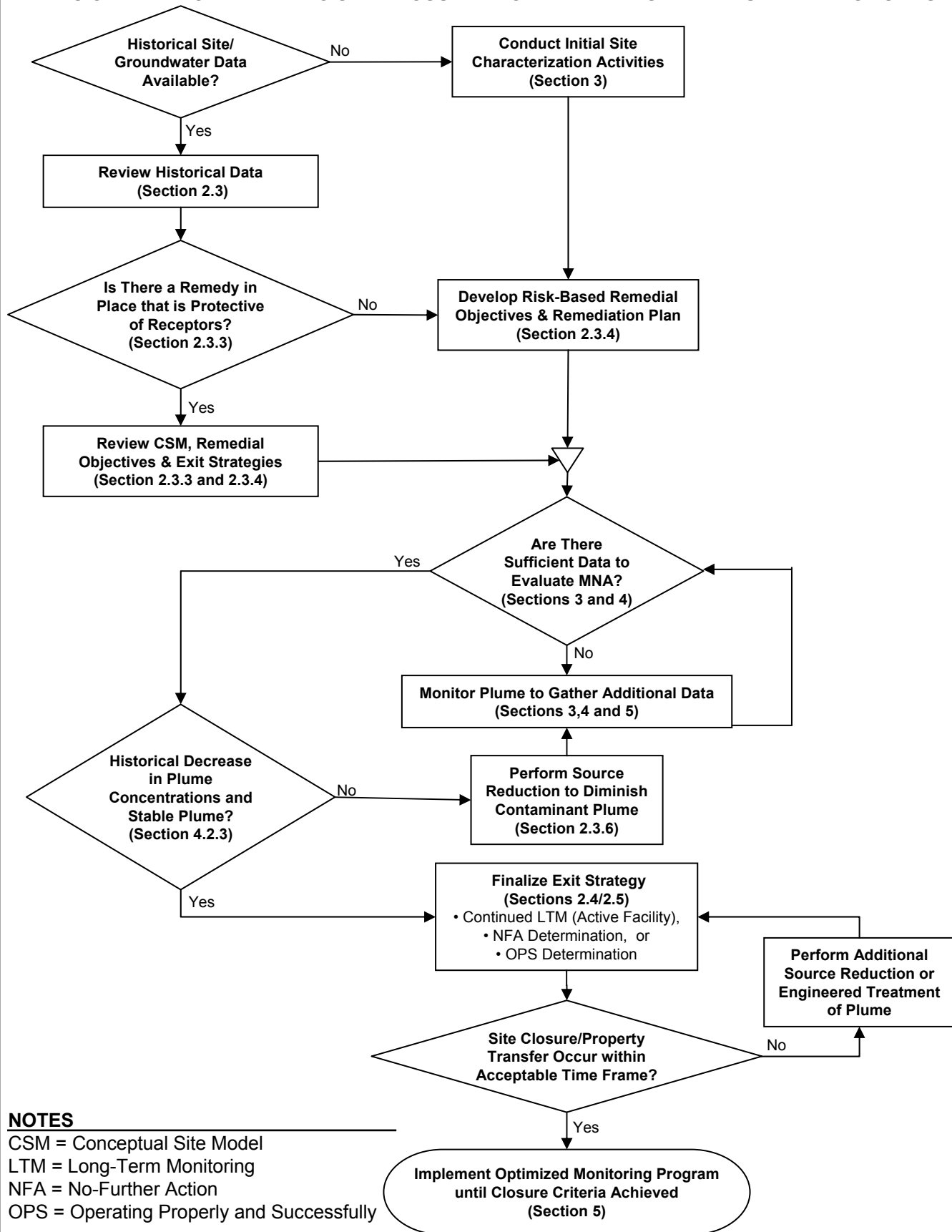
provides the user with a guide to tools that can be used to support MNA evaluation and incorporation into the site closure strategy. Many fuel sites now have multiple historical sampling events that can be used to demonstrate that the BTEX plume is stable or receding, and that concentrations are decreasing. A lack of receptor exposure risk and strong historical evidence supporting MNA should reduce the need for additional sampling, plume modeling, and extensive geochemical analysis. These sites should be advanced as site closure candidates or documented as "Operating Properly and Successfully" if the land is to be transferred to non-DoD owners.

2.2.3   Cost-Effective Source Reduction When Required

At sites with a significant LNAPL plume or high concentrations of contaminants in the soil or ground water, natural attenuation processes alone often are too slow to reduce risk within an acceptable or 'reasonable' time frame. Note that definition of an acceptable or 'reasonable' time frame is a site-specific determination that must consider the intended future land use. For example, an acceptable time frame may be less than one year for sites that are scheduled for property transfer. At sites where the desired remediation time frame is relatively short, active source reduction technology will be required to reduce the mass of contaminants and to enhance and accelerate their natural destruction. Conversely, a 30-year (or more) time frame may be 'reasonable' for sites that are located on active facilities. At these sites, natural weathering of the LNAPL may allow attainment of remediation goals without implementation of engineered source removal. Section 4.2.2.1.6 describes methods of determining the natural rate of source weathering, which, based on experience at many DoD sites, is the single most important factor in estimating MNA remediation time frames.

Note that several cost-effective technologies have been developed and widely tested by the USAF to meet the need for source reduction. The USAF bioventing initiative demonstrated that bioventing was effective at reducing BTEX concentrations in soil by an average of 95 percent when applied for one year (AFCEE, 1996). SVE and dual phase extraction have been equally effective in removing BTEX concentrations from more volatile fuels such as gasoline (USEPA, 1997b). The USAF bioslurping initiative demonstrated that bioslurping technology is capable of improving the rate of mobile LNAPL recovery at many sites where other technologies have failed but also highlighted that enhanced removal rates are often a short-term benefit (AFCEE, 1997a). At sites that do not have expensive infrastructure, excavation and removal of LNAPL-impacted soil may be the most effective source reduction method, particularly if state regulations allow this excavated material to be used as landfill cap material. The reader is directed to the AFCEE website and specifically to the *Air Force Handbook for Remediation of Petroleum Contaminated Sites* (AFCEE, 1998) for additional information on how to select the most appropriate source reduction technology for a specific site.

2.3   IMPLEMENTING A SITE CLOSURE STRATEGY

This subsection provides a generic strategy for site closure at fuel-release sites, and is intended to expand on the decision tree illustrated on Figure 2.1. This strategy should be modified, as necessary, to meet site-specific needs based on land use and unique regulatory requirements.

2.3.1   Evaluating Historical Data

Historical data are particularly valuable in establishing evidence of natural attenuation processes, which may be limiting contaminant migration and reducing long-term risks. Site contaminant concentration data should be organized by environmental medium (e.g., soil, soil

vapor, ground water) and arranged in a tabular format. A site map should be available showing sampling locations, historical BTEX plumes, key land uses, potential receptors, and surface features.   Section 3 provides additional guidance on collecting and organizing site characterization information. Existing data should be sufficient to answer the following key questions:

- Where is the primary source of the contamination?

- Has the source been removed or the leak stopped?

- Is the date of release known or was it a long-term (i.e., chronic) leak?

- What media have been impacted (soil, ground water, soil vapor, surface water)?

- Are there any immediate risks to human health or the environment?

- Are there any potential risks (currently or in the future) due to soil vapors (indoor air concern), excavation (direct contact and ingestion concern), ground-water migration (drinking water or dermal contact concern), or contamination reaching surface water (direct contact concern)?

- Does a mobile LNAPL plume remain at the site (based on existing monitoring wells)?

- Has the geology (including soil/bedrock stratigraphy) been characterized?

- Have the ground-water flow direction and seepage velocity been determined?

- Has the full extent of soil and ground-water contamination been delineated?

- Does historical data indicate that the ground-water plume is expanding, stable or receding? (see Section 4)

- Have basic geochemical parameters been measured? (see Section 3)

If any of these questions cannot be answered, additional site characterization will likely be required before site closure can be pursued. The recommended protocol for site characterization activities is described in greater detail in Section 3, and Appendix D provides a summary of recommended procedures that can be used to collect the data described in Section 3.

Note on Source Identification. Because many fuel-release sites are located in active fuel handling areas, the possibility of continuing leaks must be thoroughly investigated. Regular tank and pipeline testing will be required to evaluate whether there are ongoing fuel releases that are contributing to soil and ground-water contamination. The site MAJCOM Liquid Fuels manager should be consulted to determine the most appropriate leak testing method for each specific system. The recent move towards replacement of underground piping with aboveground piping should greatly reduce the potential for undetected leaks; however, small leaks are inevitable in any large fuel handling facility.   Often these small leaks are naturally attenuated before contaminants migrate from the site.

2.3.2   Determining Current and Future Receptors/Land Use

An important aspect of the initial site evaluation is an understanding of current and future land use at the site. A site walk should be scheduled with the facility manager to determine the types of buildings constructed near the site and the frequency and type of human activity. Because risk-based remediation methods rely on a clear understanding of how humans or ecological receptors could be exposed to chemicals (exposure pathways), it is essential to have a complete knowledge of the current land use and potential land-use changes.

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For example, most USAF fuel systems are located in the industrial or commercial areas of the base. On-site workers typically work 8- to 12-hour shifts inside buildings or outside, often working on aircraft or support equipment. In many cases, exposure of on-site workers to contaminated soils is generally limited to excavations for short-term utility repairs. At these facilities, most buildings are constructed on above-grade concrete slabs that generally reduce the risk of exposure to vapors in indoor air. Current land use near fuel spills is generally industrial or commercial, with little chance of direct exposure to contaminated soil, soil vapor, or ground water. This isolation of workers from site contamination (i.e., lack of completed exposure pathways) is an important element of the remediation strategy for active USAF bases.

On installations that are scheduled for closure or realignment, the question of future land use becomes more critical. While most base flight-line and industrial areas on closure bases will remain in this land use, formal deed or lease restrictions must be in place to ensure that the new landowner (private or public) understands the extent of remaining fuel contamination and the need to restrict certain future activities or land uses. When possible, Air Force Real Property Agency (AFRPA) officials should seek risk-based closures of fuel-contaminated sites that make appropriate use of deed restrictions to minimize the potential for future human exposure to contaminants.

2.3.3   Review the Conceptual Site Model

The review of historical site data and potential land uses/receptors can be combined to update or create the site CSM. Although the complexity of the CSM will vary by site, there are three common elements of all CSMs: a definition of the source, potential pathways for exposure (e.g., ground water, soil, soil vapor, surface water), and an understanding of current and potential future receptors. <u>The reduction or removal of risk can be accomplished by limiting or removing any one of these three elements from the site.</u> The goal of risk-based remediation strategies is to find the most cost-effective method of reducing present and future risk by combining three risk reduction techniques:

- **Contaminant Source Reduction** - Achieved by natural attenuation processes over time or by engineered removals such as limited excavation, SVE, bioventing, dual-phase extraction, or bioslurping;

- **Contaminant Pathway Elimination** - Examples include natural attenuation processes in dissolved ground-water plumes that reduce COC concentrations to below applicable standards prior to reaching receptors; and

- **Restrict Receptors** - Land and ground-water use controls can eliminate chemical exposure until natural attenuation or engineered remediation reduces the contaminant concentrations at the point of contact to below applicable standards.

Figure 2.2 illustrates a CSM for a typical jet fuel release in an industrial area. The primary contaminant source is a leaking UST; the secondary source is the soil contaminated with residual jet fuel. Potential exposure pathways include direct soil contact, soil vapor inhalation, or dermal contact with impacted shallow ground water. The only potential completed receptor pathway in this industrial scenario is intrusive construction or utility workers who will have a limited exposure time frame resulting in limited risk. Note that one potential pathway that is frequently overlooked is the exposure of site workers to soil vapors during excavation activities. The inappropriate exclusion of this potential pathway from the CSM may lead to a common data gap in that there may be insufficient soil vapor data to quantify the concentration of specific volatile

FIGURE 2.2
LIMITED INDUSTRIAL EXPOSURE PATHWAY CONCEPTUAL SITE MODEL

Possible Site Sources	Affected Media	Release Mechanisms/ Migration Pathways	Exposure Routes		Potential Receptors
	Soil	• Direct releases of contaminants into soils. • Contaminants volatilizing into the atmosphere. • Disturbance of contaminated soils by excavation. • Leaching of contaminated soil into ground water.	Human	• Incidental ingestion. • Dermal contact. • Inhalation of volatilizing contaminants. • Inhalation of fugitive dust.	Current → • Onsite construction workers. Future → • Onsite construction workers.
• Fuel leaks from USTs.			Ecological		• No exposed populations, due to industrial land use
	Groundwater	• Direct releases of contaminants into ground water. • Downgradient migration of site contaminants.	Human	Dermal contact.	Current → • Onsite construction workers. Future → • Onsite construction workers.
			Ecological		• No exposed populations, due to industrial land use

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organic compounds (VOCs; e.g., BTEX) and evaluate potential inhalation risks to on-site workers.

Figure 2.3 illustrates a CSM for a leaking UST located in a more accessible commercial area such as a Base Exchange (BX) Service Station. Potential exposure pathways include soil contact or ingestion, soil vapor migration to the atmosphere (or buildings), incidental contact with shallow ground water, and direct contact or incidental ingestion of impacted surface waters. Potential receptors include on-site workers, adult and child vistors to the BX, and ecological receptors in the nearby surface water. This CSM indicates a greater risk may be present at this site due to greater potential for receptors to be exposed through multiple pathways. The MNA evaluation at this site would focus on the potential for plume migration and discharge to surface water, resulting in impacts to human or ecological receptors.

To be conservative, the CSM should account for all possible pathways and receptors given the current and likely future land uses. At military facilities scheduled for closure, the future land use may differ from the current land use. In such situations, the most conservative expected land use should be used to develop the CSM. Unless residential land use specified in the future land use plan, it is reasonable to assume that future land use will be industrial or commercial in areas of the facility that have been historically used for this purpose. Appendix C provides additional discussion on the components and methodology used to develop a site-specific CSM.

2.3.4 Develop Site-Specific Remedial Objectives

At most sites, regulatory agencies will require that the responsible parties achieve numeric cleanup goals before final site closure can be granted. There are several specific circumstances where achievement of numeric cleanup goals may be needed to move the site closure process forward:

- Sites for which local regulations require cleanup to specific numeric criteria;

- Sites with completed exposure pathways that require more immediate reductions in soil or ground-water contamination; or

- Sites where future land/ground-water use controls and excavation restrictions can not be guaranteed.

In each of these situations, establishment and application of site-specific remedial objectives should result in a more attainable closure agreement and limited LTM requirements. This section describes the key steps in selecting and establishing site-specific, risk-based remedial objectives.

The RBCA process involves a tiered approach in which assessment and resultant remediation activities can be tailored to site-specific conditions and risks (ASTM, 1995a). Increasingly complex levels of data collection and risk evaluation may be performed to establish the type and magnitude of remediation required to reduce or eliminate unacceptable risks at a particular site. The tiered approach provides the flexibility to replace potentially overly conservative, generic exposure assumptions with site-specific information, while still providing the same level of human health and environmental resource protection. Three basic tiers of site evaluation (e.g., data analysis) have been established in the RBCA process:

- Tier 1 or screening-level evaluations;

- Tier 2 or site-specific evaluations; and

- Tier 3 or advanced site-specific evaluations.

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FIGURE 2.3
MULTIPLE EXPOSURE PATHWAY CONCEPTUAL SITE MODEL
FOR A TYPICAL AIR FORCE FUEL RELEASE SITE

Prevailing Wind Direction

Former UST

Volatilizing VOCs

On-Site Worker

Contaminated Soil

Drainage Culvert

Surface Water

Shallow Groundwater

Possible Site Sources | **Affected Media** | **Contaminant Release Mechanisms, Migration Pathways and Attenuation** | **Exposure Routes** | **Potential Receptors**

Soil
- Direct releases of contaminants into soils.
- Leaching of surface spills into subsurface soils.
- Surface erosion/deposition of contaminated soil by either water or wind.
- Contaminant natural attenuation (e.g. volatilization, biodegradation)
- Disturbance of contaminated soils by excavation.
- Leaching of contaminants into ground water.

Human
- Incidental ingestion.
- Dermal contact.
- Inhalation of volatilizing contaminants.
- Inhalation of fugitive dust.

Current → Onsite workers.
Future → Onsite workers.

Ecological
- Surface soil is not contaminated.
→ No exposed populations.

Ground Water
- Direct releases of contaminants into ground water.
- Leaching of surface spills into subsurface soils
- Downgradient migration and natural attenuation of site contaminants.
- Contaminants volatillizing into vadose zone soil.
- Migration and discharge of contaminated ground water into off-base surface water.

Human
- Dermal contact.

Current → Onsite construction workers.
Future → Onsite construction workers.

Ecological
→ No exposed populations, due to industrial land use

Possible Site Sources:
- Fuel leaks from transfer and supply and return pipelines.
- Fuel leaks from USTs.
- Surface spills/overfills.

Surface Water
- Surface runoff of precipitation.
- Discharge of contaminated ground water into surface water.
- Discharge of leachate into surface water.

Human
- Incidental ingestion.
- Dermal contact.

Current → Onsite workers.
Future → Onsite workers.

Ecological
Future → BIOSCREEN modeling predicts no discharge at concentrations> surface-water criteria

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Due to the volatility and relatively high water solubility of the BTEX compounds, these constituents are among the most mobile fuel compounds and can be rapidly transported through the soil and groundwater. (See Appendix A for additional discussion on the mobility of typical COCs from fuel releases.) MNA at most fuel sites is focused on limiting the movement and reducing the concentration of BTEX compounds in the environment. In some states, MtBE has been identified as a regulated COC, although the health risks posed by exposure to this compound are continuing to be investigated.

Remediation of BTEX and PAHs in ground water should be based on site-specific risk reduction objectives and should not default to drinking water standards. Most state UST regulations have adopted several ground-water cleanup standards based on actual land use over the plume. For example, under an industrial land use scenario where only utility workers might come in contact with fuel-contaminated ground water, a benzene cleanup standard of 200 µg/L may provide adequate risk protection. In contrast, most states would require remediation on the order of 1 µg/L to 5 µg/L if the ground water was considered a drinking water source. A complete description of how risk-based, site-specific remedial objectives can be developed is beyond the scope of this document. The reader is referred to the *Air Force Handbook for Remediation of Petroleum Contaminated Sites* (AFCEE, 1998) and state regulatory guidance for information on developing these site-specific remedial objectives.

2.3.5   Evaluate the Contribution of Natural Attenuation

If existing contaminant concentrations exceed risk-based cleanup goals, the impact of natural attenuation processes should be fully documented and factored into the evaluation. In addition to demonstrating that the dissolved contaminant plume is stable, the rate of biodegradation should be estimated to support estimation of the time of remediation, as described in Section 4.2.2.1.6. Section 4 provides additional details on how to evaluate and document the effectiveness of natural attenuation.

Analytical models such as BIOSCREEN (USEPA, 1996a) and SourceDK™ (GSI, 2004) have been developed by AFCEE to predict the time frame to obtain remedial objectives and the impact of natural attenuation processes on exposure pathway completion and exposure-point concentrations over time. In addition, the United States Navy has recently funded the development of a simple numerically-based model (Natural Attenuation Software [NAS]) that uses source and contaminant degradation properties to estimate the time of remediation (Chapelle *et al.*, 2003).

Predictions about contaminant fate over time and development of cleanup goals that are protective of human health and the environment must be based on verifiable field evidence of natural chemical attenuation. The time frame for achieving risk-based cleanup goals (levels of risk reduction) should be factored into long-term land use decisions. The estimated time of remediation can also be used to provide an approximate time frame for the required duration of LTM activities. If MNA data indicate that the plume is stable and concentrations of BTEX are decreasing below site-specific, risk-based criteria, the site may be ready for closure based on a lack of exposure risk and migration. If the time frame and cost of long-term MNA is excessive or does not meet other time-constraints (e.g., property transfer), source reduction options should be considered.

2.3.6   Implement Source Reduction as Needed

There are several situations for which source reduction should be used to more rapidly or efficiently attain remedial objectives:

- There is an immediate risk to site workers due to explosive fuel vapors or vapors which are migrating into an occupied work space;

- There is a high probability that soil excavation will take place in soils that contain contaminant concentrations that exceed risk-based cleanup goals for the direct-contact, incidental ingestion, and/or inhalation exposure pathways;

- The ground-water plume is expanding and moving toward an important water resource (e.g., drinking water well or surface water); or

- The timeframe for natural attenuation alone to decrease soil and ground-water contamination below risk-based cleanup goals is unacceptably long.

As discussed in Section 2.2.3, there are a variety of source reduction methods available for fuel-release sites including: bioventing, SVE, excavation, and bioslurping to remove free and residual product. Additional information on how to evaluate the need for source reduction and select an appropriate technology is provided in Section 3 and Appendix D of the *Air Force Handbook for Remediation of Petroleum Contaminated Sites* (AFCEE, 1998).

2.3.7   Determine Monitoring Requirements

Ground-water monitoring for MNA must be sufficient to 1) demonstrate that unacceptable migration is not occurring toward potential receptors and 2) track the progress of MNA toward achieving site-specific remedial objectives. This will generally require a network of wells consisting of a combination of upgradient, source area, in-plume, and sentry wells located downgradient of the leading edge of the plume (AFCEE, 2000c). Time and experience have shown that the recommendations provided in the original protocol (AFCEE, 1995) appropriately describe how to design simple and effective LTM plans for MNA performance monitoring at fuel-release sites. Based on this experience, the recommendations in the original protocol should be used to develop simple, straight-forward LTM programs for MNA at fuel-release sites. In cases where an existing or proposed LTM program seems excessive when compared to the recommendations of the original protocol, Section 5 provides guidance on how to optimize the LTM program to achieve the goals described in the original protocol. Excessive monitoring (including geochemical analysis) should not be required once the mechanisms of biological degradation have been established during the initial site characterization. In addition, the LTM plan should be reevaluated as the dissolved ground water plume recedes over time,, such that the monitoring network gradually can be simplified to fewer wells that are sampled less frequently and analyzed for fewer analytes. To facilitate this periodic evaluation of LTM requirements, the LTM plan should clearly state the specific objectives of the monitoring program and provide a description of the criteria that need to be met before LTM can be reduced or eliminated.

2.3.8   Contingency Plans

Despite significant improvements in MNA modeling and predictive tools, there may be situations where MNA fails to provide the required level of ground-water remediation at a site. The most likely failure of an MNA-based remedy will occur in the source area, where contaminated soil or LNAPL may continue to act as a source of unacceptably elevated concentrations of BTEX or other COCs. A less likely scenario of feature for an MNA-based remedy is the continued migration of the plume toward potential receptors, particularly if the receptor is outside the base boundary. In both of these situations, a contingency plan should be in place as a part of the site closure strategy. Typical contingency plans include use of more-aggressive source reduction technologies or increased monitoring of sentry wells to confirm that BTEX concentrations are not impacting downgradient receptors.

2.4   SITE CLOSURE OR "NO FURTHER ACTION" DOCUMENTATION

There are three types of site data that should be collected in preparation for final site closure documentation or a No-Further-Action (NFA) determination at fuels MNA sites. First and foremost is a demonstration that ground-water concentrations have achieved site-specific cleanup goals. This will normally require one or two years of quarterly or semi-annual monitoring data at key wells to demonstrate that BTEX concentrations remain below the cleanup goals.

Second, the data must demonstrate that the plume is stable and no longer migrating, and that the downgradient receptors are not at risk from future migration. This can best be demonstrated using a plume map showing historical isoconcentration contours, as described in Section 4.2.2.1.1. Depending on applicable regulatory requirements, it may be possible to limit the development of these isoconcentration contour maps to benzene data, as the relatively high mobility and toxicity of this contaminant typically drives remediation objectives at many sites.

Finally, the site closure document should describe the current land use and any institutional controls that need to be maintained to prevent completion of new exposure pathways (such as restrictions on new ground-water production wells). In some states, the base commander may be required to certify that land-use controls will be maintained to preserve the validity of the exposure assumptions that allowed the use of less-restrictive cleanup standards. For sites that will be transferred to non-DoD landowners, the next section describes additional documentation that may be required before land transfer can take place.

2.5   LAND TRANSFERS ON CLOSURE BASES

2.5.1   Operating Properly and Successfully Determination Requirements

In 1992, Congress enacted the Community Environmental Response Facilitation Act (CERFA) to clarify Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Section 120(h)(3) language regarding remedial actions at federal facilities that are scheduled for closure/property transfer. Specifically, CERFA states that federal property can be transferred to non-federal parties…

> *"…if construction and installation of an approved remedial design has been completed and the remedy has been demonstrated to the EPA Administrator to be operating properly and successfully."*

The intent of this legislation was to speed the transfer of closed military installations to local governments and developers while giving USEPA Regional Administrators the responsibility for determining if the existing remedy is performing as designed and can be expected to meet final cleanup goals. This legislation applies to both National Priorities List (NPL) and non-NPL sites where final (not interim) remedial actions are underway. Resource Conservation and Recovery Act (RCRA) corrective actions that are the "sole and final response" for a site are also covered under these land-transfer guidelines (USEPA, 1996b).

According to USEPA (1996b) guidance,

> *"The phrase 'operating properly and successfully' involves two separate concepts. A remedial action is operating "properly" if it is operating as designed. That same system is operating 'successfully' if its operation will achieve the cleanup levels or performance goals delineated in the decision document. Additionally, in order to be successful, the remedy must be protective of human health and the environment…"*

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"... Because EPA must make a present judgment about the future performance of a response action, federal agencies are expected to present sufficient evidence supporting their contention that all remedial action necessary at the site has been taken."

The interim *EPA Guidance for Evaluation of Federal Agency Demonstrations that Remedial Actions are Operating Properly and Successfully* (USEPA, 1996b) provides a more detailed listing of "core criteria" that must be achieved to obtain an Operating Properly and Successfully (OPS) approval at MNA sites. In summary, the core criteria for obtaining OPS approval at MNA-based remedies at fuel-release sites will include:

- Completion of source removal or the construction of the source-control portion of the remedy. For example, an OPS determination for plume remediation by MNA was approved by regulators for a former fire training area at Brooks AFB, Texas following the use of SVE for source reduction. While experience to date has shown that virtually all state regulations have historically required some form of product recovery to have been attempted before the "source removal box" can be checked off, an OPS determination similar to that received at the Brooks AFB site should be possible if soil residuals sampling data can be used to demonstrate that quantifiable reduction in COCs was the result of natural weathering. As of the publication of this document, the authors are unaware of any examples of OPS being granted for a fuel-release site where LNAPL was observed to be present and the sole source reduction measure was natural weathering.

- Presentation of ground-water data that indicates MNA is performing as expected to include:

  - Documentation that contaminant levels have been reduced and a rate of reduction has been established;

  - The dissolved contaminant plume is stable or receding; and

  - Geochemical indicators confirm that contaminant degradation is occurring.

- Appropriate institutional controls are in place.

- Any modeling studies that were required to support the determination of a stable or receding plume are confirmed by field data and predict that cleanup objectives will be obtained within the predicted timeframe and before contaminants reach human or environmental receptors.

- The monitoring system has been completed in accordance with the approved design and is providing data needed to evaluate the progress of natural attenuation.

2.5.2   Monitoring Requirements

As indicated by the OPS core criteria, more-comprehensive historical concentration data and a periodic reevaluation of MNA may be required at sites that will be transferred while the MNA remedy is on-going. Several years of monitoring data may be required to satisfy the OPS core criteria for MNA sites. For this reason, many AFRPA site managers have opted for more-active forms of remediation at fuel-release sites. Although implementation of engineered remedial actions may result in more-rapid land transfer, these actions are also likely to have a higher economic cost and may not result in achievement of final site closure any faster than would have occurred if an MNA-alone remedy had been implemented.

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SECTION 3

RECOMMENDED PROTOCOL FOR SITE CHARACTERIZATION

The primary objective of an MNA evaluation is to determine whether naturally-occurring processes are, or are likely to, adequately contain and treat fuel-related COCs to concentrations that are below applicable cleanup goals prior to completion of a receptor exposure pathway. This section describes the rationale and recommended procedures for gathering site-specific data that should be used to support evaluation of the MNA alternative. Presentation, visual representation, and techniques for analyzing the data recommended for collection in this section are described in Section 4. Although the types of data collection recommended in this section may also be useful for the evaluation of other remedial alternatives, this section is not intended as a comprehensive guide for data collection in support of the evaluation of alternatives or technologies other than MNA. In addition, this section is not intended to replace or otherwise alter applicable regulatory requirements for site characterization.

3.1   PURPOSE AND SCOPE OF SITE ASSESSMENT ACTIVITIES

Part of the evaluation process for establishing MNA as an appropriate and suitably protective site exit strategy is to gather site characterization information that can be used to develop a scientifically-defensible argument in support of MNA. At sites where investigations have previously been performed, it is likely that some of this information has already been collected and documented as part of the RI process. The types of RI data that are useful as part of an MNA evaluation can be broadly divided into two categories: site setting and nature and extent of contamination. In addition to these general types of information, MNA-specific data will need to be collected and analyzed. **Table 3.1** provides a listing of several questions that need to be answered and information that should be gathered in advance of performing analysis of MNA-specific data.

As described in Sections 1 and 2, the primary objective of data collection for the evaluation of the MNA alternative is to provide evidence of dissolved contaminant mass loss and resulting plume stability, and to demonstrate LNAPL source control or elimination (i.e., the first line of evidence in the USEPA [1999a] directive). In cases where insufficient historical data exist to demonstrate plume stability and the sustainability of natural attenuation processes through data representation and simple analysis techniques, a secondary objective for an MNA evaluation is to provide evidence of the dominant natural attenuation processes and contaminant degradation rates (i.e., the second line of evidence in the USEPA [1999a] directive). Only at sites where these first two lines of evidence are inconclusive should additional site-specific data collection and/or analysis be necessary to allow prediction of the future extent and concentration of a contaminant plume through solute fate and transport modeling. Considering the wide variety of redox conditions that BTEX and other fuel-related COCs have been shown to biodegrade under(e.g., Suarez and Rifia, 1999), and the challenges of translating biodegradation rates from the bench-scale to the field-scale, the use of laboratory microcosms to demonstrate COC

TABLE 3.1
SITE CHARACTERIZATION DATA USED DURING MNA EVALUATION

Data Category	Examples of Specific Data Needs

Site Setting	• Surface features
	    ○ Geographic location of site
	    ○ Location, type, and use of buildings or other structures
	    ○ Location and type of overhead and underground utilities
	    ○ Location, type, and use of surface water bodies
	• Climatic conditions (e.g., temperature, precipitation)
	• Potential receptors
	    ○ Drinking water supplies (ground water and surface water)
	    ○ Non-potable water supply usage (ground water and surface water)
	    ○ Surface water bodies
	    ○ Utility maintenance/Construction activities
	    ○ Land and Ground-Water Use
	        ▪ Current
	        ▪ Future
	• Hydrogeology
	    ○ Stratigraphy
	        ▪ Identification of transmissive zones
	        ▪ Identification of confining units
	        ▪ Grain size distribution and soil classification
	    ○ Ground-water hydraulic information
	        ▪ Estimate for hydraulic conductivity and porosity
	        ▪ Hydraulic gradient (magnitude, direction, seasonal variation)
	        ▪ Recharge from or discharge to surface water bodies?
	        ▪ Identification of preferential flow paths

Nature and Extent of Contamination	• Source (LNAPL) condition
	    ○ Nature of release
	        ▪ Catastrophic spill or gradual release of LNAPL?
	        ▪ More than one source area possible or present?
	        ▪ Divergent or coalescing plumes?
	    ○ Release abated or continuing source?
	    ○ Chemical composition of release(s) and identification of COCs
	    ○ Mobile or residual LNAPL present?
	    ○ Location and thickness of mobile/residual LNAPL
	    ○ Source removal planned/completed?
	• Contaminant concentrations in air
	    ○ Indoor air (primarily basements, if any)
	    ○ Soil vapors at land surface
	    ○ Soil vapors during excavation
	• Contaminant concentrations in soil/sediment
	    ○ Residual LNAPL
	    ○ Mass/concentration of sorbed contamination
	• Contaminant concentrations in surface water
	    ○ Detectable contaminant concentrations?
	    ○ Surface water quality parameters impacted?
	• Dissolved contaminant concentrations in ground water
	    ○ Redox condition
	    ○ Biological condition

MNA-specific Data Needs	• Physicochemical properties of COCs
	• Historical data
	    ○ Source (LNAPL) weathering
	    ○ Dissolved contaminant concentrations
	• Ground-water quality evaluation
	    ○ Indicators of redox condition and biological activity
	    ○ Physiochemical ground-water quality indicators

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degradation and/or to estimate biodegradation rates is uncommon and typically of limited value for MNA evaluations at fuel-release sites.

3.2 PRE-MOBILIZATION OPTIMIZATION OF SITE CHARACTERIZATION EFFORT

The purpose of optimizing characterization efforts prior to mobilization is to: 1) avoid unnecessary costs that would arise from duplication of previous data collection efforts and 2) realize the most benefit from installation of new data points and/or performance of analytical methods that are available for supporting the MNA alternative. A recommended process for achieving this pre-mobilization optimization is to: 1) review available site data, 2) develop a preliminary CSM which includes appropriate MNA processes (see Appendix C), and 3) identify specific DQOs that can be used to test and refine the CSM through evaluation of the collected data.

3.2.1 Review Available Site Data

The first step in preparing for an MNA evaluation should be a review of available site data to determine if existing information is adequate to support determination of whether MNA is a viable remedial option. A thorough review of available data will also aid in the development of a preliminary CSM (if one does not exist) or refinement of an existing CSM (as needed). As discussed in Section 2.3.3, a comparison of available data with the CSM will help identify data gaps, and will allow placement of additional data collection points (if needed) in a scientifically-advantageous and cost-effective manner.

3.2.2 Develop Preliminary Conceptual Site Model

After reviewing existing site characterization data, a preliminary CSM should be developed, and a preliminary assessment of the potential for MNA should be made. (See Figures 2.2 and 2.3, and Appendix C for a discussion of recommended components that should be included in a CSM at typical USAF fuel-release sites). When preparing for data collection in support of quantitative evaluation of MNA, an important part of the CSM is an accurate representation of the LNAPL source and the spatial relationship of this LNAPL source to air, soil, ground water, and surface water. The impact of the LNAPL source on each of these media should be based on the chemical properties of the COCs (see Appendix A) and available hydraulic, biological, geochemical, climatological, and analytical data for the site. This portion of the CSM is important to data collection because it guides both the selection of media (i.e., air, soil, water) that may require sampling and the type(s) of MNA-specific evaluations that are necessary for a particular site.

3.2.3 Align Proposed Data Collection with Data Quality Objectives

Application of the DQO process described by USEPA (2000) is recommended as a way to develop a plan that specifies data collection of the correct type, quality, and quantity to support defensible site decisions and provide the basis for MNA evaluation. DQOs are qualitative and quantitative statements that translate non-technical (e.g., social, economic, or regulatory) project goals into technical, project-specific decision goals. During site characterization activities, these project-specific decision goals should be used to develop the sampling and analysis plan for supplemental site characterization and data collection activities related to the evaluation of MNA as a remedial alternative.

A seven-step DQO process flowchart is presented in USEPA (2000). Site-specific DQOs are developed in the first six steps of the process; these DQOs define the purpose of the data collection effort, clarify what the data should represent to satisfy this purpose, and specify the

requirements for the quality of information to be obtained from the data. The results of the first six steps of the DQO process are subsequently used in the seventh step to develop a data collection design that meets all performance criteria. Although these steps are largely intuitive, many can be, and are often, overlooked if a specific framework is not used.

Quantitative DQOs express decision statements using numbers, while qualitative DQOs express decision statements without specifying them in a quantitative manner. For example, a DQO statement for a field program that is designed to evaluate dissolved contaminant plume stability could be:

- Determine, with greater than 95-percent confidence, whether the trend of ground-water contaminant concentrations as increasing, decreasing, or no change.

To meet the objective of a particular DQO statement, specific data needs should be identified and articulated. For the above DQO statement, examples of specific data needs could include:

1. Are there a sufficient number of data points to calculate a statistically significant data trend?

2. Is the period of measurement sufficiently long to support future predictions of plume stability?

These types of data needs address the decision statements that are developed during implementation of the DQO process. The decision statements and data needs are used to develop the performance monitoring program for a MNA remedy.

An advantage of using the DQO process is that it facilitates development of monitoring objectives that are clearly stated and accompanied by specific, quantifiable performance criteria, thereby enhancing the usefulness of the supplemental site investigation program. The DQO process provides a systematic approach for defining the criteria that a data collection design should satisfy, including:

- When, where, and how to collect samples or measurements;

- Determination of tolerable decision error rates; and

- The number of samples or measurements that should be collected.

The ultimate goal of the site investigation program for collecting data to support MNA evaluation and the DQO process are one and the same: to collect data of the correct type, quality, and quantity to support defensible site decisions.

3.3 SOURCE AREA CHARACTERIZATION

The release of fuels to the subsurface environment will lead to contamination of soil, soil vapor, and, in many cases, ground water. During the downward migration of fuels as an LNAPL, individual fuel components will partition to the various media (air, soil, water) based on the chemical characteristics described in Appendix A, and the LNAPL chemical composition will 'weather' over time. Understanding the nature, extent, and weathering characteristics of the fuel-release source area is critical to an MNA evaluation because the persistence and strength of contaminant release to soil vapor and ground water has generally been found to be the most important factor to estimating the timeframe for achieving remedial endpoints.

At sites where an RI already has been performed, contaminant concentration data for soil, soil vapor, and ground water will have been collected as part of the effort to define the nature and extent of contamination. In addition, RI activities will have also identified whether there is

mobile LNAPL present. The purpose of the discussion in this section is to describe what types of data are needed to assess source characteristics that, particularly with respect to source weathering mechanisms, are important to an MNA evaluation. Following the discussion of source area characterization data needs, Section 3.3.2 provides a general description of source area characteristics, the factors that influence LNAPL migration and source weathering, and the potential uses of soil vapor data. Section 3.3.3 describes parameters that can be measured in and around the source area to evaluate source strength and weathering characteristics, with additional supporting information on source area data collection provided in Section D.1 of Appendix D.

3.3.1 Data Needs for Source Area Characterization

The following data types can aide in the evaluation of the extent and condition of contaminants in the source area of fuel-release sites:

- Characteristics of the fuel release;
- Lithologic description of the unsaturated zone, including identification of low permeability zones which may constitute barriers to downward LNAPL migration;
- COC concentrations in soil and soil vapor; and
- Soil moisture content.

In addition, the following types of information can be used to help assess the weathering characteristics of a mobile LNAPL plume, if present:

- LNAPL plume thickness;
- Ground-water velocity;
- Distance from the source area; and
- VOC concentrations in the LNAPL.

3.3.2 Source Area and LNAPL Characteristics

The size, persistence, and strength of the contaminant source are important for understanding the nature, extent, and anticipated duration of soil, soil vapor, and ground-water contamination at fuel-release sites. The size, geometry, and chemical characteristics of the source area are governed by the nature of the fuel release, properties of subsurface materials in the unsaturated zone, and the physical and chemical characteristics of the LNAPL (Mercer and Cohen, 1990; Pfannkuch, 1984). The primary fuel-release characteristics that influence the size and geometry of the source area are the volume, rate, and area of the release, and the density and viscosity of the LNAPL (Hunt *et al.*, 1988). Physical soil properties that influence the source geometry and LNAPL migration include lithology, soil permeability, pore size distribution, porous media wettability, fluid pressure at and above the water table, and water table fluctuations. Chemical composition of the source area (and resulting contamination of other media) is dependent on the fuel composition and the effects of source weathering on individual fuel components. The following discussion describes the factors influencing source geometry and weathering in further detail. In addition to the brief discussion of LNAPL weathering mechanisms provided here, the reader may wish to refer to published information by Parsons (2003) and Huntley and Beckett (1997) for more information.

3.3.2.1 Factors Influencing Source Geometry and LNAPL Migration

Following LNAPL release into the unsaturated (vadose) zone, LNAPL will move downward through the unsaturated zone under the force of gravity. **Figure 3.1** provides a schematic

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FIGURE 3.1

SCHEMATIC OF LNAPL RELEASE SCENARIOS, WEATHERING MECHANISMS, AND CONTAMINANT MIGRATION PATHWAYS

Small-Volume Release of LNAPL
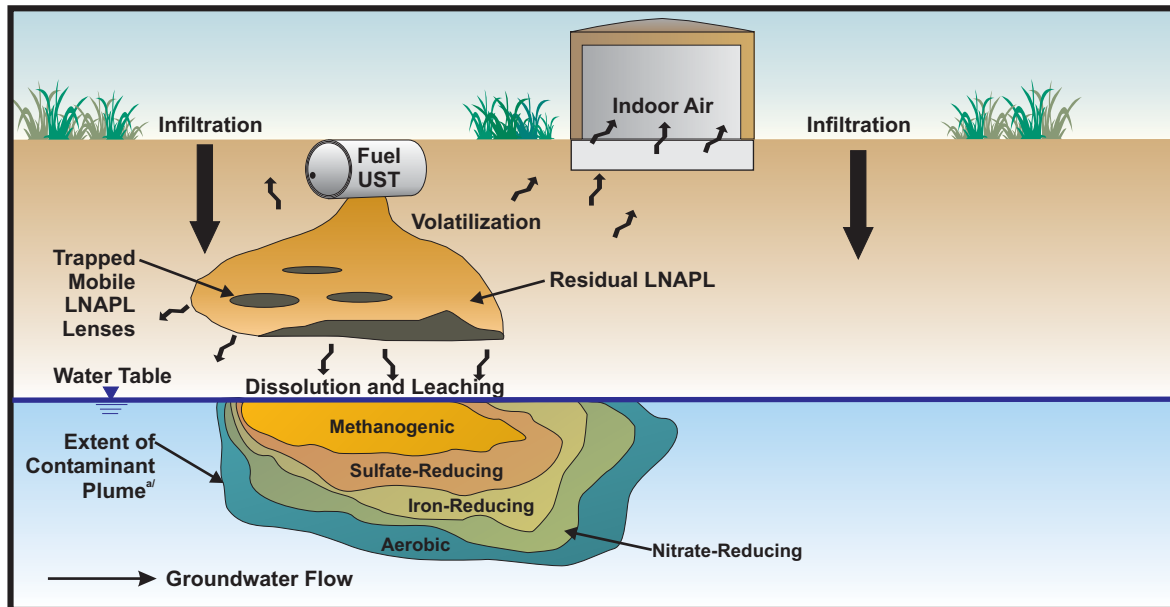
Large-Volume Release of LNAPL

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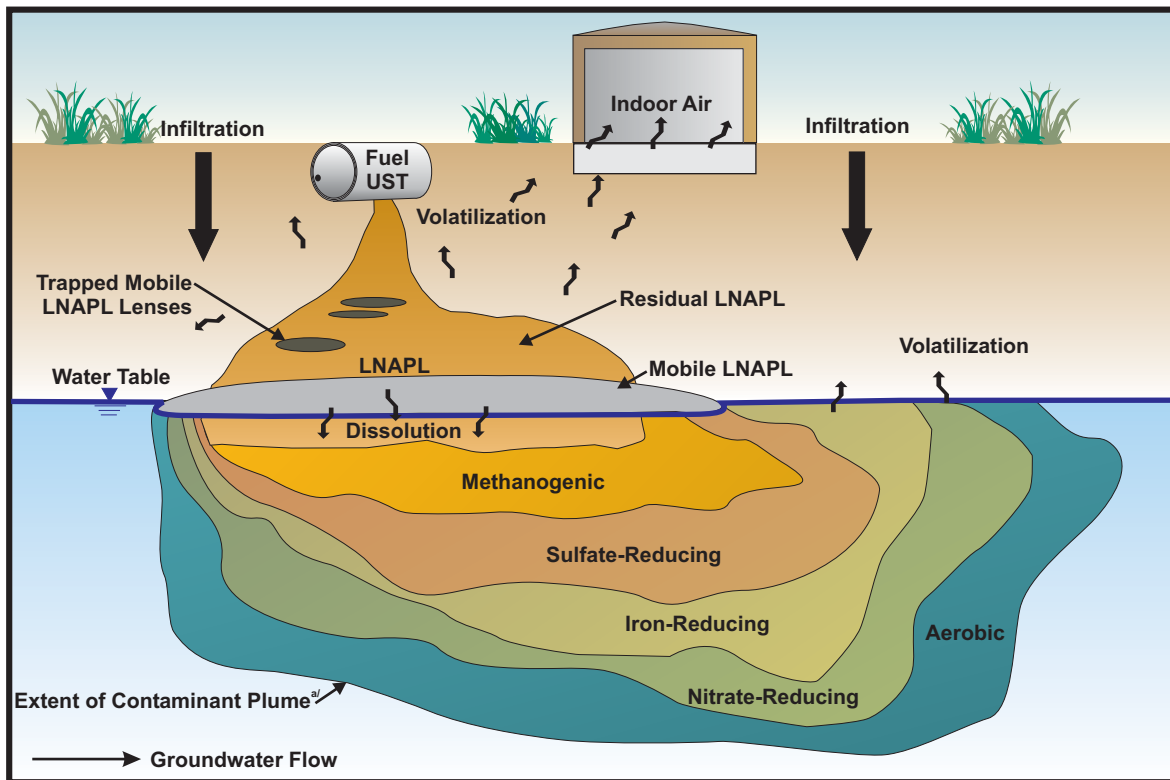
[a/] Typical Sequence of Biological Activity Zones Shown within Contaminant Plume

representation of the anticipated differences between contaminant distribution and affected media for a small and large volume LNAPL release at a typical USAF maintenance facility. Heterogeneities in soils of the unsaturated zone may cause lateral spreading and trap lenses of LNAPL above layers of low-permeability soils during downward migration. In addition, interfacial forces (e.g., surface tension at the interfaces between soil, air, water, and LNAPL) and soil capillary forces can cause residual masses of the LNAPL to become trapped in soil pores as ganglia and lenses (Hunt *et al*., 1988; Powers *et al*., 1991; Seagren *et al*., 1993). If the volume of the fuel release is relatively small and/or the depth to ground water is great, the entire LNAPL volume may be retained in soil pores as residual LNAPL and may not reach the water table. In this case, mobile LNAPL would not accumulate on top of the water table, and the necessary measurements for source characterization may be limited to collection and analysis of contaminants found in soil and soil vapor If the volume of release is sufficiently large (or the water table is relatively close to the point of release), LNAPL may accumulate at either the water table or in areas of the vadose zone where low permeability materials (e.g., clay) are present above the water table. In this case, quantification of LNAPL plume characteristics will be required in addition to soil and soil vapor characterizations activities to estimate the mass of contaminants remaining in the subsurface, and the anticipated duration of release of COCs to ground water and/or soil vapors. Because the residual LNAPL can remain trapped in the unsaturated zone for an indefinite length of time (often on the order of decades to centuries), residual LNAPL may serve as a long-term source of ground-water contamination during infiltration and/or fluctuations in the water table that bring ground water into contact with the residual LNAPL (Abriola and Pinder, 1985; Seagren *et al*., 1993).

3.3.2.2   Source Composition and LNAPL Weathering Mechanisms

Chemical composition of the LNAPL will vary over time, as source weathering will cause individual fuel constituents to partition out of the LNAPL and into either the vapor, sorbed, or aqueous phases at rates that are a function of the chemical properties of the particular fuel constituent. The term "weathering" refers to the reduction of the more volatile and mobile compounds in LNAPL over time. LNAPL weathering is caused by the combined effects of destructive (e.g., biodegradation) and non-destructive (e.g., volatilization) processes to reduce the persistence, mobility, mass, and toxicity of mobile constituents (e.g., BTEX, MtBE) following the fuel release to the environment. **Figure 3.2** provides a schematic illustration of how these weathering mechanisms act upon LNAPL in the subsurface. As shown in Figure 3.2, the primary mechanisms acting to reduce the mass and concentration of an LNAPL source are dissolution, biodegradation, and volatilization.

Dissolution occurs when chemical mass is transferred from LNAPL into ground water and/or infiltrating precipitation water. At fuel-release sites, partitioning of the most soluble compounds (i.e., BTEX and MtBE, when present) from LNAPL into ground water represents the most significant source of ground-water contamination. LNAPL dissolution is governed by the characteristics of the aquifer matrix (including effective porosity and ground-water velocity), physical properties of the LNAPL (e.g., surface area of the LNAPL in contact with ground water), and characteristics of the specific LNAPL contaminant (e.g., effective water solubility) (Parsons, 2003).

Biodegradation of dissolved petroleum contaminants enhances LNAPL weathering through increased dissolution of soluble compounds from residual LNAPLs to ground water by increasing the concentration gradient between the LNAPL and dissolved phases (Seagren *et al*., 1993; Yang *et al*., 1995). Although biodegradation of neat LNAPL (i.e. pure free product) in

FIGURE 3.2

MECHANISMS OF LNAPL WEATHERING

Monitoring Well

Residual LNAPL

Trapped LNAPL Lenses

Fuel UST

Dissolution Leaching

Volatilization

Volatilization

Water Table

Product Smear Zone

Range of Water Table Fluctuations and Resulting Product "Smear Zone"

Dissolution

Mobile LNAPL

Biodegradation of Dissolved Contamination

Extent of Dissolved Contamination

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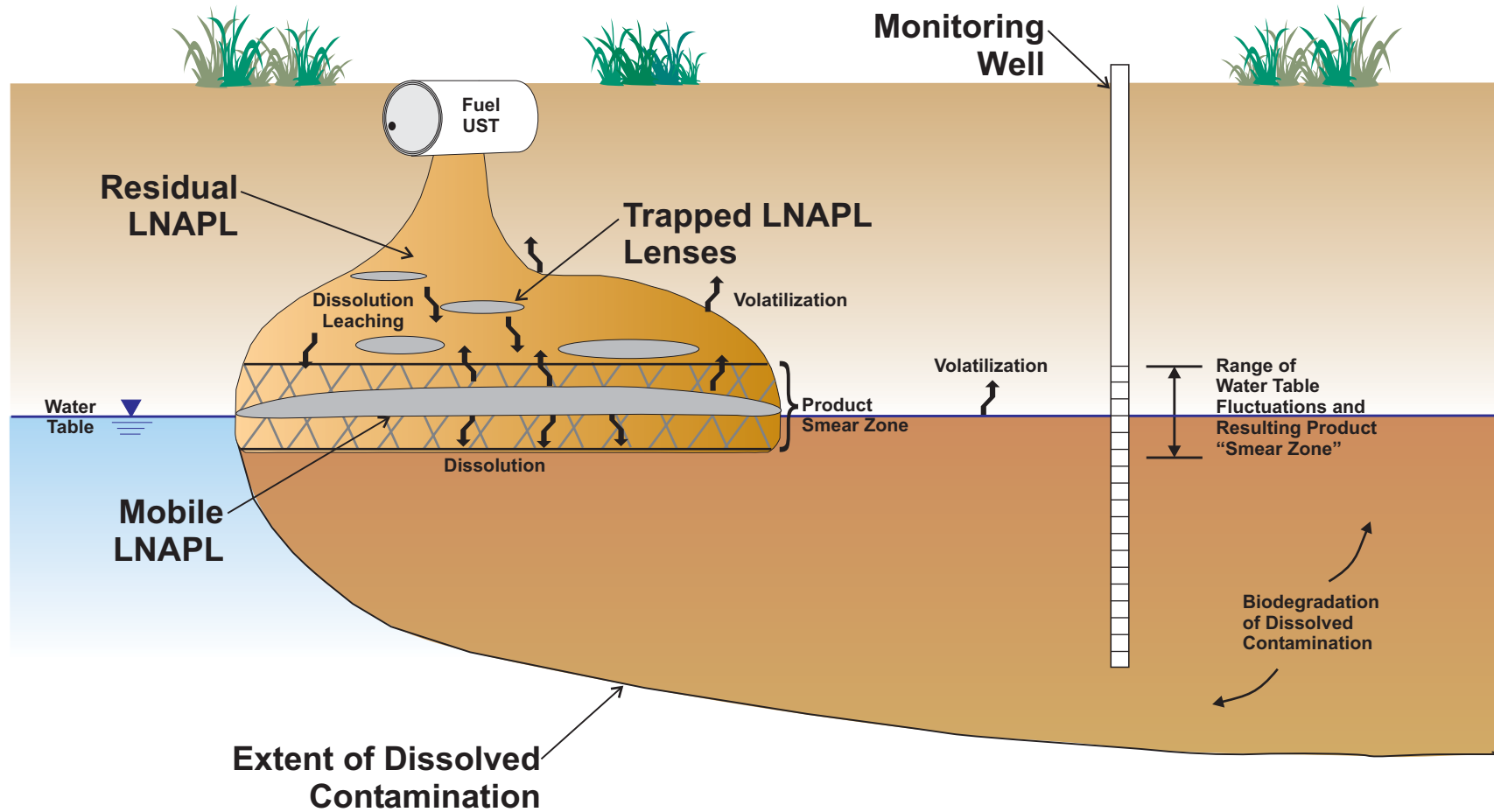
tanks has been demonstrated, *in situ* biodegradation of LNAPL has not been observed in the field (Newell *et al.*, 1995). Two plausible explanations of why *in situ* biodegradation of LNAPL may not occur to a measurable extent are that 1) typical soil microbes may not be able to maintain cell integrity in a LNAPL and 2) requirements for microbial activity (e.g., nutrients, terminal electron acceptors, moisture, osmotic potential) may not be able to migrate into (or be replenished at a sufficient rate in) the LNAPL plume (Huling and Weaver, 1991). Consequently, the effects of bioremediation are expected to occur primarily in the dissolved plume and periphery of the LNAPL, if present.

Volatilization, or evaporation, is the transfer of a compound from a liquid or solid state to a vapor state. In terms of LNAPL weathering, volatilization is a non-destructive mechanism that transfers volatile fuel components from LNAPL to soil vapor. For surface spills, important factors affecting volatilization include temperature, vapor pressure of the individual LNAPL constituents, and wind speed. For subsurface releases, important factors affecting volatilization are temperature, vapor pressure, soil moisture, and soil porosity (LaGrega *et al.*, 1994). Investigations by Hillel (1980) demonstrated that volatilization was directly proportional to soil porosity, pore size distribution, and temperature; but inversely proportional to volumetric moisture content. Although each of the mechanisms described above will contribute to source weathering, results of a recent AFCEE study on LNAPL weathering at fuel-release sites suggest that dissolution is the rate-limiting factor in LNAPL weathering, especially as it relates to biodegradation of the most soluble LNAPL constituents (Parsons, 2003). The physical parameters that can be used to help quantify the effects of source weathering include LNAPL thickness, local ground-water velocity, soil/aquifer material, and distance from the source area. These factors are expected to impact BTEX depletion within mobile LNAPL. Measurement techniques for physical and chemical parameters that will allow for estimates of source weathering are discussed in the Section 3.3.3.2.2.

For mobile LNAPLs, *LNAPL thickness* at the interface of the unsaturated and saturated zones is believed to influence BTEX dissolution from the LNAPL (Huntley and Beckett, 1997). For example, dissolution modeling of a 10-centimeter (cm) LNAPL thickness in fine sand indicated that the effective solubility of benzene could be reduced to approximately 0.001 milligrams per liter (mg/L) in less than a year. However, modeling results for a 50-cm LNAPL thickness indicated it would take approximately 70 years to reach the same effective solubility (Huntley and Beckett, 1997). As indicated by these findings, it is expected that a thicker mobile LNAPL zones will retard the rate of benzene (and presumably other highly soluble compound) dissolution from the mobile LNAPL. Note also that LNAPL thickness measurements from ground-water monitoring wells are not indicative of LNAPL thicknesses in the formation (Blake and Hall, 1984; Hall *et al.*, 1984; Hughes *et al.*, 1988; Testa and Paczkowski, 1989; Farr *et al.*, 1990; Mercer and Cohen, 1990; Huntley *et al.*, 1994). Mercer and Cohen (1990) suggest that the measured LNAPL thickness in wells is typically 2 to 10 times greater than the LNAPL thickness in the formation. In addition, depiction of mobile LNAPL as a distinct layer present above the water capillary fringe has been challenged by research conducted by Farr *et al.* (1990). For example, Huntley *et al.* (1994) indicate that hydrocarbon-saturated soil layers may not exist at sites with measurable LNAPL; rather, LNAPL and water coexist in soil pores at residual LNAPL saturations ranging up to 40 to 50 percent. In either case, the thickness of LNAPL within a soil column is expected to influence LNAPL weathering rates. Methods for measuring LNAPL thickness are described below in Section 3.3.3.2.1.

In areas where either residual or mobile LNAPL is in direct contact with ground water, contaminant partitioning from the LNAPL into ground water increases with *ground-water*

velocity. In soil column experiments performed by Miller *et al*. (1990), the rate of mass transfer between a toluene LNAPL and the aqueous phase was found to be directly related to the aqueous-phase flow velocity. In addition, equilibrium conditions between the two fluid phases were rapidly achieved over a wide range of test conditions. Considering these findings, it is reasonable to assume that sites with higher ground-water velocities would be expected to exhibit more rapid BTEX depletion of LNAPLs that are in contact with ground water. Section 3.4.2.1 provides discussion and references for methods of estimating ground-water velocities.

The *type of soil/aquifer material* at a fuel-release site is expected to influence both mobile and residual LNAPL weathering primarily as a result of fluid distribution and migration. Wettability, or the tendency for one fluid to spread on or preferentially coat a solid surface in the presence of another fluid with which it is immiscible, is impacted by the presence of organic matter, mineralogy, and saturation history of the porous medium (Mercer and Cohen, 1990). Capillary pressure also impacts the configuration and magnitude of trapped residual LNAPL and is a function of soil pore size (Newell *et al*., 1995). LNAPLs have been observed to preferentially migrate through sands and gravels, rather than silts and clays, providing direct evidence that larger pore sizes will tend to be conducive to an increased rate of LNAPL migration and dissolution (Newell *et al*., 1995).

Field observations suggest *distance from the point of release* or other spatial variability may be observed in LNAPL weathering rates (Landon and Hult, 1991). This observation suggests that data to support weathering rate calculations should be collected from multiple locations across the LNAPL plume. Potential explanations for why weathering rates may vary spatially include: 1) differences in time of release (and, therefore, duration of weathering), 2) increased surface area in areas of residual saturation, and 3) increased effects of biodegradation on aqueous concentrations at the periphery of the LNAPL, which may produce larger concentration gradients and result in LNAPL weathering rates that are faster at the LNAPL plume periphery than in the interior of LNAPL plume.

3.3.2.3   Potential Uses of Soil Vapor Data

The decision on whether to collect additional soil vapor characterization data (to supplement measurements made during RI or other site investigations) should be made based on the intended objective of these measurements. The following discussions are provided to assist users of this document in deciding whether to conduct additional soil-vapor surveys.

3.3.2.3.1   Soil Vapor Screening as an LNAPL or Dissolved VOC Plume Delineation Method

Characterization of fuel-related VOCs in soil vapor can be a valuable method for defining areas where mobile or residual LNAPL are present in the subsurface. Soil vapor surveys also can be used for preliminarily delineation of the dissolved fuel plume in ground water at some sites. In either case, the results of these soil vapor screening surveys may be helpful in selecting installation points for either temporary or permanent wells.

Soil vapor screening is widely used to evaluate spatial patterns of contamination by VOCs (Kerfoot, 1988; Martin and Kerfoot, 1988; Brock, 1990; Byrnes *et al*., 1990; Rivett, 1995). Soil vapor screening programs are typically conducted in the early phases of site investigation (e.g., during the RI) to rapidly and cost-effectively identify areas where high concentrations of volatile fuel-related compounds are present. The advantages of soil vapor screening programs over conventional soil or ground-water sampling programs are that:

1. Large amounts of data can be collected relatively quickly and inexpensively; and

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2. Given that soil vapor screening results are generally obtained in real time in the field, soil vapor screening programs can be flexible and iterative in that the selection of the next monitoring point can be based on the results of previous measurements.

Initial sampling points are placed in known or suspected source areas or spill areas based upon historic data review, and samples are collected and analyzed in the field in near real-time. Successive sampling points are located based upon the results of the previously-collected samples with the objective of determining the location and extent of detectable VOC contamination in soil vapor.

Potential drawbacks of soil vapor screening include:

1. Results of such a program are generally considered to be qualitative or semi-quantitative and have been categorized as "screening-level" data. As such, most regulatory agencies will not accept soil vapor concentrations as a method of compliance monitoring. To gather quantitative data acceptable to regulators, soil vapor screening programs are generally followed by a direct soil characterization and monitoring well installation program.

2. Delineation of subsurface contamination via soil vapor sampling can be complicated by the presence of fine-grained soils and/or excessive soil moisture, which can hamper migration of vapor-phase contaminants, and the presence of low-permeability (e.g., pavement) caps which cause vapor-phase VOCs to migrate laterally beyond the limits of the contaminated area.

At sites where the release location and contaminant source area are reasonably well-known (e.g., where it is known that the release came from a particular UST), performance of a soil-vapor survey may not be useful. In these cases, it may be most efficient and cost-effective to move directly into collection of soil samples and/or ground-water samples using a hand auger, conventional drill rig, or direct-push techniques (DPT). A soil-vapor survey will be most applicable at larger sites where the contaminant source(s) and/or extent of subsurface contamination are poorly defined.

The DQOs for a "follow-on" soil and ground-water sampling program should include: 1) validation of results from the soil vapor screening program and 2) improved delineation and quantification of the nature, magnitude, and extent of subsurface contamination (i.e., soil, ground water, and mobile LNAPL). Soil, mobile LNAPL, and ground-water characterization programs are discussed in more detail in Sections 3.3.3.1, 3.3.3.2, and 3.4, respectively. In addition, Appendix D contains guidance on sampling techniques.

3.3.2.3.2   Soil Vapor Characterization to Determine Potential Exposure

As described in Section 2.3, concentrations of selected fuel-related VOCs (generally BTEX) in soil vapor should be quantified to assess the potential for impacts to receptors (e.g., vapor migration into occupied buildings or excavations). Vapor-intrusion pathways often dominate risk assessments at sites where the potential for ground-water ingestion has been eliminated (Schultz, 2003). The ground-water ingestion pathway generally outweighs the vapor-intrusion pathway because cleanup standards for ingestion pathways are typically lower than for vapor-intrusion pathways (Schultz, 2003). Accordingly, the topic of vapor intrusion has been of increasing interest in recent years (USEPA, 2002b). Note that assessment of the soil vapor exposure pathway will be less important at sites where fuels with relatively low VOC concentrations (e.g., diesel fuel, heating oil, motor oil, JP-8) were released. It is critical for ground-water modelers and risk assessors to indicate whether plume migration predictions

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suggest that a plume may migrate beneath areas that currently or may, in the future, have residential or commercial/industrial use with confined subgrade spaces (Schultz, 2003).

At previously-characterized sites, an assessment of receptor exposure to contaminants in soil vapor during current and anticipated future land use should have been performed as part of the RI process. If the findings of the risk assessment indicate unacceptable risk to current or potential future receptors, use of MNA of contaminants in the area of exposure as the sole remedial measure is not likely to be appropriate unless institutional controls (e.g., land-use restrictions) are put in place to protect potential receptors. However, if an engineered remedial technique (e.g., SVE) is used to address soil vapor contamination, MNA may still be a potential remedial option for ground water and should be evaluated. If risk-based calculation of receptor exposure to soil vapor has not been performed at a site, this analysis should be performed before (or in coordination with) the MNA evaluation.

Because a soil vapor sampling program that is intended to provide data for use in evaluating potential impacts to receptors needs to be quantitative (rather than qualitative), the DQOs and scope of this type of program will tend to differ from those developed for a soil vapor screening program of the type described in Section 3.3.2.3.1. The quality assurance/quality control (QA/QC) portion of a quantitative soil vapor sampling program is generally more substantial than that of a soil vapor screening program, and should be clearly defined and incorporated into the DQO process.

An indoor air-quality sampling program will likely be required for any buildings or other structures that overlie the area of mobile and/or residual LNAPL contamination. USEPA (2002b) has recently provided draft guidance that may be helpful when developing a monitoring program for soil vapor intrusion into indoor air. In addition, the Massachusetts Department of Environmental Protection (2002) provides indoor air sampling guidance. Alternatively, analytical models (e.g., Johnson and Ettinger, 1991) have been developed to facilitate prediction of indoor air quality based on measured concentrations of VOCs in soils. This model has been modified to include first-order biodegradation for a dominant soil layer (Johnson *et al*., 1998) and oxygen-limited first-order biodegradation (Roggemans *et al*., 2001). Based on comparison of measured and model-predicted (e.g., Johnson/Ettinger model) indoor air concentrations at multiple sites, Hers *et al*. (2003) concluded that the Johnson/Ettinger model (or other similar screening models) can be reliably used to assess the vapor intrusion pathway provided that appropriate input values are used and the model sensitivity, uncertainty, and limitations are recognized. In addition, *Risk-Based Corrective Action Applied at Petroleum Release Sites* (ASTM, 1995a) includes an analytical screening-level model for estimating the transport of contaminant vapors from subsurface sources into indoor air. This model has been used in the development of six spreadsheets, which are available from the USEPA website (USEPA, 2003b).

3.3.2.3.3 Soil Vapor Characterization to Support an MNA Evaluation

Although not commonly performed at most fuel-release sites, soil vapor analysis for carbon dioxide, oxygen, and methane provides a qualitative method of demonstrating biodegradation of fuel constituents in the vadose zone. Detection of high concentrations of carbon dioxide and low concentrations of oxygen in soil vapor, with respect to atmospheric concentrations, suggests that there is significant biological activity in the area of sample collection. The detection of high soil vapor concentrations of methane indicates that methanogenesis is occurring, and that geochemical conditions are highly reducing. Due to the qualitative use of soil vapor analyses for oxygen, carbon dioxide, and methane, analysis for these soil vapor parameters is not generally recommended unless there is a specific need to demonstrate to regulators or other stakeholders

that biodegradation of fuels is occurring in the unsaturated zone. In these limited cases, soil vapor data that suggests increased biological activity in source areas, relative to background (i.e., non-impacted) conditions, can provide a scientifically-defensible indication that biodegradation of fuel-related compounds is occurring in the source area.

3.3.3 Defining Relevant Contaminant and Physical Characteristics of the Source Area

The nature, magnitude, and 3-D extent of the fuel-release source area should be documented and quantitatively evaluated during initial or supplemental site characterization activities using a combination of soil and residual LNAPL sampling, measurements of mobile LNAPL properties, and collection of soil vapor samples. These source area characterization activities are necessary to evaluate the nature and extent of contamination, and to evaluate the timeframe for source abatement. Establishing the nature and extent of the source area and contaminated soil vapors, in conjunction with understanding dissolved contaminant plume dynamics (as discussed in Section 3.4), is important for identifying: 1) current or potential future risks to human health and the environment and 2) whether additional source reduction activities are needed to expedite the rate at which the plume is diminishing in terms of extent and/or concentration.

At sites where the source area is entirely contained within the unsaturated zone (i.e., no mobile LNAPL accumulation at the water table), the source area investigation should focus on residual LNAPL and soil vapor measurements, as needed to supplement existing information. At sites containing mobile LNAPL, additional measurements of LNAPL thickness and composition, along with hydrogeologic information, such as ground-water velocity, also should be evaluated. The following subsections briefly describe methods for measuring chemical or physical properties of soil, residual LNAPL, mobile LNAPL, and soil vapor in the event that existing source characterization data is not sufficient to support an MNA evaluation. As part of this discussion on the protocol for source area characterization, recommendations on the TAL for each medium are provided. Additional details regarding source area media sampling, analysis, and QA/QC procedures are provided in Section D.3 of Appendix D. Note that the procedures described in this document may require modification on a site-specific basis to comply with local, state, and federal regulations.

3.3.3.1 Soil and Residual LNAPL Characterization

Characterization of soil properties and the nature, extent, and magnitude of residual LNAPL contamination (commonly referred to as "soil contamination") in the source area is discussed in this subsection. For fuel releases, the source area will extend vertically from the point of release (generally a location in the unsaturated zone) down to, and including, a fuel "smear" zone that will develop from seasonal fluctuations in the water table (e.g., McKee *et al.*, 1972; Dietz, 1980; Schwille, 1984; Voudrias *et al.,* 1994). As described in Appendix C, residual LNAPL includes contaminants that are sorbed to soil particles or present as droplets trapped between soil particles (i.e., occluded).

The distribution of LNAPL in the unsaturated and smear zones can be highly variable, with residual LNAPL present as discrete ganglia (Hunt *et al*., 1988). Characterization of residual LNAPL is important because it impacts 1) estimates of the longevity of the source of ground-water and soil vapor contamination, 2) assessment of risks to potential receptors, and 3) evaluation of the persistence and migration potential of the dissolved contaminant plume.

3.3.3.1.1 Soil Sampling and Collection Methods

Soil samples can be collected through the use of conventionally-drilled (e.g., augered) soil borings or borings advanced using DPT (e.g., Geoprobe® or cone penetrometer testing [CPT]).

Geologic/hydrogeologic investigation and data analysis methods have been well described in other documents, such as the descriptions of drilling methodologies described by ASTM (1995b through 1995h, 1997, and 1998b) and USEPA (1991). Users of this protocol are encouraged to refer to these resources for additional information on conventional drilling techniques. Similarly, soil sampling techniques have also been well described by others, such as USEPA (1995a and 2001b) and ASTM (1998b, 2001a, and 2003). In addition, Appendix D provides additional supporting information regarding drilling and soil sampling procedures.

Since the publication of the original protocol (AFCEE, 1995), experience using DPT for soil sampling at many sites has shown this method to be cost-effective for collecting soil samples, while concurrently minimizing generation of investigation-derived wastes (IDW) that require special handling, characterization, and disposal. As an alternative to collecting actual samples, DPT-compatible devices have been developed that provide a continuous log of soil characteristics and selected classes of contaminants. These technologies are designed to provide rapid sampling in real-time and relatively low-cost analysis of the physical and chemical characteristics of subsurface soil to quickly distinguish contaminated areas from uncontaminated areas. For example, the Membrane Interface Probe (MIP®) is a tool developed for logging VOCs in the subsurface. It can be driven to depth using Geoprobe® percussion soil probing equipment. The Site Characterization and Analysis Penetrometer System (SCAPS®) Laser Induced Fluorescence (LIF) sensor developed by the Tri-Services (United States Army, United States Navy, and USAF) for use with CPT, was found to be capable of reliably mapping the relative magnitude and vertical and horizontal extent of subsurface contamination, when that contamination is fluorescent (Bujewski and Rutherford, 1997a). This type of contamination includes petroleum fuels and PAHs. The Rapid Optical Screening Tool (ROST®) is another CPT-compatible LIF sensor developed by Loral Corporation and Dakota Technologies, Inc. to provide real-time field screening of aromatic petroleum hydrocarbon contamination at fuel-release sites (Bujewski and Rutherford, 1997b). Use of screening-level sensors such as the MIP, SCAPS, and ROST will be most cost-effective on relatively large sites where subsurface conditions are conducive to use of DPT, and where extensive conventional drilling would be required to adequately characterize the source area.

3.3.3.1.2   Geology in the Unsaturated Zone

Because LNAPL migration is driven by gravity, lithologic, stratigraphic, and structural features typically dominate LNAPL movement in the subsurface. Any boreholes advanced for soil sampling and/or monitoring well installation also should be used to obtain lithologic descriptions of subsurface materials in both the unsaturated zone (for investigating LNAPL migration) and the saturated zone (for investigating preferential flow paths and estimating ground-water velocities and retardation factors, as described in Section 3.4). When evaluating unsaturated zone transport, the observation of fine-grained layers within coarser-grained material should be incorporated into the CSM because layers of relatively finer-grained material have the potential to inhibit downward NAPL migration, resulting in significant quantities of fuel being retained in the unsaturated zone. In this case, the unsaturated zone may be expected to act as a long-term source of ground-water contamination because contaminants may slowly "bleed" into ground water over many years if source reduction technologies are not implemented.

3.3.3.1.3   Soil Analytical Protocol

The recommended analytical protocol for soil sample analysis is presented in **Table 3.2**. This analytical protocol includes a list of parameters that are recommended for documenting MNA of

TABLE 3.2 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING SOIL, MOBILE LNAPL, AND SOIL VAPOR AT FUEL-RELEASE SITES [a/]

Analysis	Method/ Reference	Comments	Data Use	Potential Data Quality Concerns
Soil				
Total petroleum hydrocarbons (TPH; includes GRO, DRO, and oil and grease)	SW8015M [b/]	Regulatory requirements and analytical methods for TPH vary by state. State requirements should be reviewed prior to selection of TPH analytical method.	• Determination of extent of petroleum contamination in soil; • Determination of the total petroleum-related contaminant mass present in the soil matrix; and • Evaluation of the need for source removal.	• Sampling results are dependant upon sampling methodology and soil type; • Soil heterogeneity will affect the reproducibility of analytical results; and • Potential for volatile loss during sampling and shipping; field extraction is preferred.
Aromatic hydrocarbons (e.g., BTEX, TMBs)	SW8260B or SW8021B	Standard USEPA analysis methods	• Determination of the extent of soil contamination; • Determination of the aromatic contaminant mass present in the soil matrix; • Evaluation of the need for source removal; and • Evaluation of risk posed to potential receptors.	• Sampling results depend upon sampling methodology and soil type; • Soil heterogeneity will effect the reproducibility of analytical results; and • Potential for volatile loss during sampling and shipping; field extraction is preferred.
Total organic carbon (TOC)	SW9060 modified for soil samples	Procedure must be accurate over the range between 0.5 and 15 percent TOC	• Determination of the rate of migration of petroleum contaminants in the vadose zone as well as within the saturated zone.	• Soil heterogeneity will effect the reproducibility of analytical results; • Sampling results are dependant upon soil type; and • Samples must be collected from contaminant transporting (i.e., transmissive) intervals.

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TABLE 3.2 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING SOIL, MOBILE LNAPL, AND SOIL VAPOR AT FUEL-RELEASE SITES [a/] (Continued)

Analysis	Method/ Reference	Comments	Data Use	Potential Data Quality Concerns
Soil (Concluded)				
Moisture	ASTM D-2216 [c/]		• Used for correction of soil sample analytical results for moisture content (e.g., report results on a dry weight basis).	• Soil heterogeneity will affect the reproducibility of analytical results; and • The results of this analysis are sensitive to sampling method.
Ferric and Ferrous Iron	Under Development (See AFCEE, 2000b for more information)	HCl extraction followed by quantification of released ferric and ferrous iron	• Optional method used to predict the potential to biodegrade fuel hydrocarbon mass via iron reduction (ferric iron); and • Optional method used to determine how much fuel has been degraded via the iron reduction pathway (ferric and ferrous iron).	• Soil heterogeneity will affect the reproducibility of analytical results; • Sampling results are dependant upon soil type; and • Samples must not be allowed to oxidize.
Mobile LNAPL				
Aromatic hydrocarbons (e.g., BTEX)	SW8260B or SW8021B		• Determination of VOC source mass remaining within mobile LNAPL; and • Determination of BTEX weathering rate.	• Results are sensitive to sample collection method; • Potential for volatile loss during sampling; and • Difficult to analyze in the lab resulting in high detection limits and increased costs.
Mobile LNAPL thickness measurements	Field interface probe		• Determination of mobile LNAPL thickness and volume; and • Evaluation of mobile LNAPL plume stability.	• Data must be collected by a trained technician to ensure data quality; • Results may be sensitive to seasonal ground-water fluctuations; and • LNAPL thickness may be sensitive to grain size.

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TABLE 3.2 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING SOIL, MOBILE LNAPL, AND SOIL VAPOR AT FUEL-RELEASE SITES [a/] (Concluded)

Analysis	Method/ Reference	Comments	Data Use	Potential Data Quality Concerns
Soil Vapor				
Screening for total volatile hydrocarbons or total ionizable VOCs	Direct-reading air monitoring instrument (PID, FID, or TVH meter)	Measured semi-quantitatively in the field using Tedlar® bag or direct reading of vapor from sampling device.	• Preliminary assessment of VOC presence in the vadose zone; and • Evaluation of LNAPL extent.	• Data collected is semi-quantitative; data useful for preliminary delineation of source zones only; • VOCs cannot be speciated; • Potential for atmospheric dilution during sampling; and • Results are affected by soil heterogeneity.
Sampling for aromatic hydrocarbons (e.g., BTEX)	USEPA TO-13A, TO-14A, TO-15, or portable field GC	Collected in a Summa Canister®, or Tedlar® bag (field GC method only)	• Evaluation of nature and extent of LNAPL; • Evaluation of contaminant concentration trends over time in soil vapor; and • Assessment of potential impacts to receptors by COCs in soil vapor.	• Potential for atmospheric dilution during sampling; • Results are affected by soil heterogeneity; and • Use of portable field GC requires a trained operator and proper calibration procedures.
Methane, oxygen, and carbon dioxide	Direct-reading field meter(s)	Measured semi-quantitatively in the field.	• Qualitative evidence of biological activity in unsaturated zone.	• Instrument(s) must be properly calibrated; • Potential for atmospheric dilution during sampling; and • Results are affected by soil heterogeneity.

[a/] Analyses other than those listed in this table may be required to demonstrate regulatory compliance.

[b/] "SW" refers to *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods, SW-846, 5th Edition* (USEPA, 1998c).

[c/] "ASTM" refers to method specified by the *American Society for Testing and Materials*.

NOTE: PID = photoionization detector; FID = flame ionization detector; TVH = total volatile hydrocarbons. BTEX = benzene, toluene, ethylbenzene, and xylene isomers; VOCs = volatile organic compounds; LNAPL = light non-aqueous phase liquid; COCs = contaminants of concern; GC = gas chromatograph.

fuel hydrocarbons, including the effects of sorption and biodegradation (aerobic and anaerobic). Each analyte is discussed separately below.

Total Petroleum Hydrocarbons

Currently, more than half of the state agencies that regulate fuel-release sites require analysis for total petroleum hydrocarbons (TPH) in soil and/or ground water. However, the "TPH" designation does not, by itself, define a standard test. Rather, this term indicates the total concentration of hydrocarbons found within the boiling range specified as part of a particular analytical method and, in some cases, following extraction by a particular solvent (TPH Criteria Working Group, 1998). As discussed in Appendix B, most states that are currently requiring "TPH" analysis actually require analysis for GRO and/or DRO, depending on the type of fuel released. GRO and DRO, which correspond to the C_6 to C_{10} and C_{10} to C_{28} ranges of alkanes, respectively, typically are measured using USEPA Method SW8015B. However, some states (e.g., Massachusetts) require use of a state-specific TPH analytical method rather than a standard USEPA method. Given the variation in requirements and methods for assessing TPH at fuel-release sites, users of this protocol are encouraged to review state- and site-specific requirements when obtaining TPH data, with the objective of ensuring that the type of sample collection and analysis performed are consistent with the requirements of the regulatory agencies charged with oversight of site remediation and closure.

Knowledge of the location, distribution, concentration, and total mass of TPH sorbed to soils, present as small droplets trapped between soil particles (i.e., occluded), or present as mobile LNAPL is used to define the boundaries of the LNAPL plume in the source area; this can be important when simulating contaminant source areas in fate and transport models.

Soil samples are typically analyzed for TPH during the initial site characterization phases only. However, some state regulatory agencies (e.g., Arizona, Texas, and Vermont) require TPH concentrations in soil to be below a specified concentration prior to site closure.

VOCs in Soil

Knowledge of the location, distribution, concentration, and total mass of fuel-derived VOCs (especially BTEX) sorbed to or occluded in soils, or present in mobile LNAPL, is required to estimate contaminant partitioning from mobile and residual LNAPL into ground water or soil vapor. Soil samples for aromatic hydrocarbons analysis are typically collected during the site characterization to determine the nature and extent of VOC contamination in soil. Most regulatory agencies have compound-specific cleanup criteria for soil; therefore, documentation that these criteria have been met (via additional soil sampling and analysis for aromatic hydrocarbons) may be required to obtain site closure.

Soil Moisture Content

Soil moisture content is an analysis that is automatically performed on soil samples that are submitted to a fixed-base laboratory for VOC analysis in cases where analytical results are reported on a dry-weight basis (i.e., performance of this analysis does not have to be specifically requested). Soil moisture content data are used by the laboratory to correct soil analytical results for moisture content by subtracting the moisture mass and reporting concentrations in terms of soil dry weight (e.g., milligrams (mg) of contaminant per kilogram (kg) of soil dry weight). Soil moisture content also can be used to infer the potential for biodegradation of fuel compounds in the vadose zone. Biodegradation of fuel compounds in vadose zone soils can proceed only if the soil particles to which the contaminants are sorbed are covered with a water film. The water film supports the microbial population that mediates

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biodegradation of fuel compounds. The presence of abundant soil moisture in the vadose zone can be inferred to represent favorable conditions for fuel-degrading microorganisms, particularly if the area is paved or otherwise capped by a low-permeability layer that minimizes evaporation, and warm temperatures that are conducive to microbial activity are prevalent.

3.3.3.2 Mobile LNAPL Characterization

As described in Section 3.3.2.1, LNAPL may accumulate at either the water table or in areas where low permeability materials are present in the vadose zone if the fuel release is of sufficient volume to reach the water table. At fuel-release sites, partitioning of BTEX compounds from LNAPL into ground water and soil vapor represents the most significant source of ground-water and soil vapor contamination, respectively. Conversely, partitioning is perhaps the most significant mechanism of BTEX depletion in mobile LNAPLs (Huntley and Beckett, 1997). This section focuses on characterizing mobile LNAPL and the relevance of this characterization to MNA evaluations.

3.3.3.2.1 LNAPL Plume Stability Measurements

LNAPL plume stability can be assessed by collecting LNAPL product thickness and ground-water elevation measurements in both source area and downgradient monitoring wells through time. During the RI phase, a monitoring well network of sufficient size to define the horizontal and vertical extent of mobile LNAPL and dissolved constituents should have been installed. This monitoring well network should be monitored for several years prior to the initiation of, or as part of, an MNA evaluation to determine if the LNAPL plume is shrinking, stable, or expanding. If the mobile LNAPL plume is shrinking or stable, then MNA may be an appropriate remedial option for the site. After MNA has been selected, plume stability will have to be monitored on a regular basis to ensure that the plume remains stable. It should be noted that the regulatory community may require removal of recoverable mobile LNAPL prior to the selection of MNA, even if the plume is shown to be stable or shrinking. It should also be noted that short-term mobile LNAPL stability studies may need to be performed to assess transient plume stability at some sites that exhibit tidal influence or strong seasonal variations in water table elevation. For example, at a site with strong tidal influence a 24- or 48-hour plume stability study may be required where LNAPL thickness measurements are collected hourly. The objective of such a short term study is to determine if the LNAPL plume is stable at all tidal stages. It should be recognized that a stable dissolved phase plume is good circumstantial evidence that the LNAPL plume is also stable.

3.3.3.2.2 Mobile LNAPL Analytical Protocol

The recommended analytical protocol for mobile LNAPL sample analysis is presented in Table 3.2. This analytical protocol includes each of the LNAPL parameters that are deemed necessary to support evaluation of MNA of fuel hydrocarbons. Each analyte is discussed separately below, with additional supporting information provided in Section D.1.3 of Appendix D.

VOC analysis of mobile LNAPL samples is important for estimating the mass of the more soluble fuel components (e.g., BTEX) that are remaining within the mobile LNAPL, and to improve the estimate of BTEX contaminant source longevity. If present, mobile LNAPL samples should be collected from several wells within the source area and shipped to a fixed-based laboratory for analysis for each sampling event. Collection and analysis of samples from multiple wells is important because weathering rates are likely to vary from well to well within the same LNAPL plume. Performance of multiple LNAPL sampling events through time is

recommended to facilitate calculation of weathering rates that more accurately represent actual site weathering conditions. Each sampling event should be conducted on the same group of wells and should be conducted relatively frequently (semi-annually or annually) if the spill is relatively new (less than 5 years old) or less frequently (annually or biennially) if the plume is relatively old (greater than 5 years). Older plumes should be sampled less frequently because they will tend to weather more slowly than a younger plume (Parsons, 2003). Mobile LNAPL sampling methodologies are discussed in Section D.1.3 of Appendix D.

After VOC concentration data in the LNAPL has been collected, a source decay model (e.g., SourceDK™, GSI [2004]) can be calibrated to measured changes in BTEX concentrations in mobile LNAPL over time. Using this calibrated model, predictions can then be used to predict the rate of VOC depletion (i.e., "weathering"), and to develop an estimate of when the LNAPL source will no longer contain significantly elevated concentrations of specific VOCs.

3.3.3.3   Soil Vapor Characterization

Characterization of the nature and extent of VOC contamination in soil vapor in the source area is important for evaluating potential impacts to receptors via the soil vapor migration pathway. Soil vapor characterization also can be used to preliminarily delineate: 1) "hot spots" of residual LNAPL contamination within the vadose zone and 2) mobile LNAPL and ground-water contaminant plumes at sites where soil is relatively permeable and ground water is relatively shallow. Soil vapor characterization and sampling techniques are described by USEPA (1995b, 1997c, and 2001b) and ASTM (2001b). A brief description of soil vapor analytical parameters, sampling methodologies, and data analysis methods relevant to an MNA evaluation is presented in this section, with supporting information provided in Section D.1.2 of Appendix D.

Recommended methods for soil vapor sample analysis are presented in Table 3.2. This analytical protocol includes multiple soil vapor parameters that can be used to accomplish the sampling objectives described in Sections 3.3.2.3. In addition to the supporting information provided in Appendix D, discussion of soil vapor screening and soil vapor sampling methods is also provided in San Diego Department of Environmental Health (2002) and ASTM (2001b). Each analyte is discussed separately below.

VOCs in Soil Vapor

Methods used for collection and analysis of soil vapor will vary depending on whether the results are intended to be used as soil vapor screening (i.e., qualitative results) or soil vapor sampling (i.e., quantitative results). Screening-level VOC analysis can be conducted with a portable, field-calibrated, direct-reading meter for total ionizable VOCs or total volatile petroleum hydrocarbons. Soil vapor screening can also be performed quantitatively in the field for a selected TAL (e.g., BTEX) using a portable gas chromatograph (GC). Soil vapor samples that are collected to assess potential exposure risks to receptors and/or to validate a soil vapor screening program are typically collected in Summa Canisters® and shipped to a fixed-base laboratory for VOC analysis using USEPA Methods TO-13A, TO-14A, or TO-15.

Carbon Dioxide, Oxygen, and Methane in Soil Vapor

Carbon dioxide, oxygen, and methane concentrations in soil vapor are typically measured in the field using a direct-reading meter. Soil vapor samples can be collected in a Tedlar® bag, which is in turn connected to the meter. Alternately, the meter can be connected directly to the top of a soil vapor sampling point and the meter's suction pump can be used to draw soil vapor into the meter for analysis. Soil vapor samples for these parameters can also be collected in

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Summa Canisters® and analyzed in a fixed-base laboratory using one of the USEPA methods listed in Table 3.2. Based on experience using both methods, the data quality obtained with a field instrument has generally been found adequate to provide a qualitative assessment of biological activity in the unsaturated zone in and around the source area.

3.4   GROUND-WATER CHARACTERIZATION

When characterizing ground-water conditions for MNA evaluation at a fuel-release site, two general categories of information are required. The first category is hydrogeologic characteristics that are used to quantify ground-water flow and contaminant transport phenomena. Section 3.4.2 provides a brief description of parameters that commonly are measured to quantify these phenomena. The second category of required information is geochemical ground-water characteristics, which are also commonly referred to as ground-water quality measurements. A description of ground-water quality parameters, including discussion of potential COCs and indicators of local redox conditions is provided in Section 3.4.3, with supporting information on sampling procedures provided in Section D.2 of Appendix D.

Hydrogeologic investigation and geochemical data analysis methods have been well described in other references. For example, aquifer testing and aquifer test data analysis methods to obtain important aquifer hydraulic information such as hydraulic conductivity are described in Driscoll (1986), Dawson and Istok (1991), Kruseman and de Ridder (1994), ASTM (1996a, 1996b), Hall and Chen (1996), Butler (1997), and Weight and Sonderegger (2001). Similarly, ground-water sampling techniques are described in AFCEE (1997b), Fetter (1999), Weight and Sonderegger (2001), USEPA (1996c and 2002c), and ASTM (2001c, 2002a, 2002b). The reader is directed to these references if further information on the subjects discussed in this section is desired.

3.4.1   Data Needs for Ground-water Characterization

Typical hydrogeology-related data needs to support MNA evaluations for fuel-release sites include:

- Lithologic descriptions of aquifers (i.e., water-transmitting zones) and aquitards (i.e., barriers to ground-water flow);

- Horizontal and vertical hydraulic gradients; and

- Hydraulic conductivity of (at a minimum) aquifer matrix materials comprising primary ground-water and dissolved contaminant migration pathways and (in some cases) low-permeability (e.g., aquitard) zones.

Typical geochemical data needs to support MNA evaluations for fuel-release sites include measurement of:

- COC concentrations dissolved in ground water; and

- Concentrations of selected redox and other physicochemcal indicator parameters (e.g., electron acceptors, metabolic byproducts).

3.4.2   Hydrogeologic Characteristics

The physical processes that control the migration of solutes in ground water at most sites are advection and hydrodynamic dispersion. In addition, several processes cause a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system; these processes include dilution, sorption, and diffusion. To determine the mass of contaminant removed from the system, it is necessary to first correct observed changes in contaminant concentrations for the effects of these processes. This can be done by incorporating

independent assessments of these processes into a comprehensive solute transport model (analytical or numerical) that is applied and calibrated to site-specific data. The following sections give a brief overview of the processes that can cause an apparent reduction in dissolved contaminant concentrations during migration of solutes in ground water (i.e., advection and hydrodynamic dispersion) or sorption. In addition, the effects of heterogeneity, anisotropy, and flow through fractured media on contaminant transport are described below.

3.4.2.1 Advective Transport

The process by which solutes are transported by the bulk motion of the flowing ground water is known as advection (e.g., Freeze and Cherry, 1979; Fetter, 1999). Advection occurs when a hydraulic gradient is present. Hydraulic gradient is defined as the change in hydraulic head (e.g., the vertical difference in water table elevation) at any two locations divided by the length of ground-water flow between these two locations. The parameter used to quantify the effects of advection is the average linear velocity (i.e., seepage velocity or average ground-water velocity), which is defined as the one-dimensional (1-D) flow that is normal to the cross-sectional area of the porous media. Two methods exist for quantifying the average linear velocity: measurement of input parameters that are substituted into Darcy's equation or direct measurement using a borehole flow meter. In the first method, average linear advective flow velocity is calculated using the following equation:

$$v = \frac{K * i}{n_e}$$

where: v = average linear velocity [L/T]

              K = hydraulic conductivity [L/T]

              i = hydraulic gradient [L/L]

              n_e = effective porosity of the water-bearing zone [-].

The input parameters for this equation can be estimated using the procedures described below.

To accurately estimate *hydraulic gradient*, it is recommended that ground-water levels be measured in all monitoring wells and piezometers at a site (typically to the nearest 0.01 foot). Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific ground-water elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in ground-water flow direction can have a profound influence on contaminant transport. Sites in upland areas are less likely to be affected by seasonal variations in ground-water flow direction than sites situated near surface water bodies such as rivers and lakes.

To determine the effect of seasonal variations in ground-water flow direction on contaminant transport, quarterly ground-water level measurements should be obtained over a period of at least one year. For many sites, these data may already exist and should be reviewed prior to initiating additional investigations into seasonal variations in ground-water velocity (direction or magnitude). If hydraulic gradient data over a one-year period are not available, MNA can still be implemented pending an analysis of seasonal variation in ground-water flow direction.

Hydraulic conductivity is a measure of an aquifer's ability to transmit water, and is perhaps the most important aquifer parameter governing fluid flow in the subsurface. The velocity of ground water and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence

contaminant fate and transport by providing preferential paths for contaminant migration. Estimates of hydraulic conductivity are used to determine residence times for contaminants and tracers, and to determine the seepage velocity of ground water.

The most common methods used to quantify hydraulic conductivity are aquifer pumping tests and slug tests. Instructions for scoping and performing these tests and analyzing the results are provided in many references, including those listed in the introduction to Section 3.4. Other methods that may be used to determine hydraulic conductivity are the borehole dilution test (Freeze and Cherry, 1979) and, as described below, ground-water/borehole flowmeters. One drawback to the pumping and slug test methods is that they average hydraulic properties over the screened interval. To help alleviate this potential problem, the screened interval of the well should be selected after consideration is given to subsurface stratigraphy. Information about subsurface stratigraphy should come from geologic logs created during borehole advancement. An alternate method to delineate zones with high hydraulic conductivity is to use hydraulic pressure dissipation data from cone penetrometer test logs.

Pumping tests generally give the most reliable information on hydraulic conductivity, but are difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated. In addition, a minimum 4-inch-diameter well is generally required to complete pumping tests in highly transmissive aquifers because the 2-inch submersible pumps available today are not capable of producing a flow rate that is large enough for meaningful pumping test results to be recorded. In areas with fairly uniform aquifer materials, pumping tests can be completed in uncontaminated areas, and the results can be used to estimate hydraulic conductivity in the contaminated area. Pumping tests should be conducted in wells that are screened in the most transmissive zones in the aquifer.

Slug tests are a commonly used alternative to pumping tests. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. A second drawback is that the commonly-used test procedure (i.e., employing manual slug insertion) may not provide accurate results in formations having medium to high hydraulic conductivity (greater than approximately 30 feet per day), because the rapid recovery of water levels can lead to significant "noise" in the early-time data and erroneous interpretation of the water-level recovery curve. In this case, use of a pneumatic slug testing method similar to that described by Renner (1993) is recommended. Slug tests do, however, have two distinct advantages over pumping tests: they can be conducted in 2-inch monitoring wells and they produce no water that requires disposal. Because slug tests provide estimates for hydraulic conductivity in the local area near the test well, multiple slug tests must be performed at several monitoring wells if slug tests are going to be used to provide information on the 3-D distribution of hydraulic conductivity in an aquifer. It is not advisable to rely on data from one slug test in one monitoring well for an estimate of overall site hydraulic conductivity. As with pumping tests, slug tests should be conducted in wells that are narrowly screened in the most transmissive zones in the aquifer.

The *effective porosity* is the porosity available for fluid flow (Fetter, 1999). Effective porosity is typically estimated based on lithologic descriptions of the water-bearing material using tables of effective porosities for various lithologies found in the hydrogeologic literature (e.g., Domenico and Schwartz, 1998; Spitz and Moreno, 1996).

An alternate method for estimating the magnitude and direction (horizontal and vertical) of local ground-water flow is the direct measurement of these parameters using one or more types of ground-water/borehole flowmeters. Flowmeters also can be used to assess the relative

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hydraulic conductivity in porous media or flow through fractured rock at discrete positions in a screened well or uncased borehole. This method also can be used to evaluate the direction of ambient vertical hydrostatic pressure gradients throughout the depth of a borehole. The work of Molz and Young (1993), Molz *et al*. (1994), Young and Pearson (1995), and Young (1995) describe some of the means by which these tests may be conducted and interpreted. In addition, internet searches on keywords such as "Groundwater Flowmeter" and "Borehole Flowmeter" yield useful additional information on a wide variety of methods, equipment, and vendors.

3.4.2.2 Hydrodynamic Dispersion and Diffusive Transport

Hydrodynamic dispersion is the sum of mechanical dispersion and molecular diffusion. Although these two phenomena are commonly combined for the purpose of contaminant transport modeling, they are produced by different processes. A solute in water will move from an area of greater concentration toward an area where it is less concentrated. This process, which is known as molecular diffusion, will occur as long as a concentration gradient exists, even if the water is not moving. Mechanical dispersion refers to the mixing process that occurs as a result of tortuous flow paths that individual water molecules follow through a porous medium at velocities that are variably greater or less than the average linear velocity. As a result of mechanical dispersion, solute concentrations at the advancing edge of the plume are diluted. At most sites, diffusion is insignificant relative to mechanical dispersion, and is neglected in solute transport analyses. However, at a small percentage of sites, the ground-water flow velocity may be sufficiently low that diffusion is the dominant hydrodynamic dispersion mechanism and is a significant contributor to overall contaminant transport. Calculation of the Peclet number for a specific site or plume can indicate whether a ground-water system is diffusion-dominated, dispersion dominated, or mixed. Use of the Peclet number approach suggests that, for BTEX compounds, the influence of diffusion-based transport should be considered as part of the evaluation of the dominant transport process in aquifers where the ground-water flow velocity is less than 30 feet per year (ft/yr). Details regarding the calculation of the Peclet number are provided in Section A.4.2.2 of Appendix A.

It is important to assess the dominant solute transport mechanisms at a site (i.e., advection and mechanical dispersion or molecular diffusion) because most commonly-used solute transport models assume an advection-dominated system. In addition, common solute degradation rate calculation methods, such as that described by Buscheck and Alcantar (1995), are not theoretically valid for diffusion-dominated systems. Fate and transport predictions for diffusion-dominated systems should be made using a diffusion-based mass transport model in which contaminant transport is dominated by concentration (rather than hydraulic) gradients. Sections 4.2.2.1.3 and 4.2.2.1.6 describe methods for estimating decay rates at sites where transport is dominated by diffusion.

3.4.2.3 Sorption

Sorption is a process by which dissolved contaminants partition from ground water and adhere to particles comprising the aquifer matrix. Sorption of dissolved contaminants results in slowing (retardation) of contaminant migration relative to ground-water velocity, a reduction in dissolved contaminant concentrations in ground water, and a corresponding increase in the mass of contaminant sorbed onto the aquifer matrix. Sorption is a reversible process that occurs when a concentration gradient exists between the dissolved and sorbed phases of a given chemical. In dynamic systems where solute concentrations change due to the effects of solute transport and/or degradation processes, the relative amount of contaminants that are sorbing and desorbing will change. Sorption does not eliminate solute mass; it merely transfers contaminants between the

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dissolved and sorbed phases, which results in an apparent retardation in contaminant migration at the edges of a contaminant plume. In most subsurface systems at fuel-release sites, chemical partitioning occurs at a rate that maintains chemical equilibrium between the sorbed and dissolved phases.

Quantification of the degree to which solute migration is retarded relative to the advective ground-water velocity (e.g., the "retardation coefficient") is essential to predicting the fate and transport of dissolved fuel contaminants in the vadose and saturated zones. Site-specific information necessary to calculate the retardation coefficient includes an estimate for the fraction of organic carbon, bulk density of the porous medium, effective porosity, and the chemical-specific organic carbon distribution coefficient (K_{oc}). Estimates for each of these input parameters should be obtained as part of normal site characterization activities, and a review of available data prior to conducting additional field investigations may provide the data necessary for the purposes of an MNA evaluation. In terms of specific measurements, the fraction organic carbon (i.e., native [or natural] organic carbon content) of the aquifer matrix material should be measured at an analytical laboratory using soil samples collected from the field. At a minimum, samples for fraction organic carbon measurements should be collected at multiple locations in the vicinity of the fuel release. If additional plume migration is anticipated, samples for fraction organic analysis should also be collected downgradient from the plume and along the primary flowpath because collection of samples from fuel-contaminated zones may result in fraction organic carbon estimates that are biased high. The concern with fraction organic carbon estimates that are biased high is that these measurements will result in retardation coefficient and sorbed mass estimates that are also biased high. Although bulk density and porosity can be estimated using literature values based on lithologic descriptions of the water-bearing materials recorded during borehole investigations, sample collection and laboratory testing to obtain site-specific data for these two parameters will result in more-accurate estimates. Values for the organic carbon distribution coefficient of the most common fuel-release COCs are provided in Table A.1 of Appendix A. Values for other ground-water contaminants are widely available in chemical handbooks. Calculation of the retardation coefficient is discussed in further detail in Section A.4.2.3 of Appendix A.

3.4.2.4   Considering Anisotropy and Heterogeneity

The term *anisotropic* is used to describe materials where a particular physical property, such as permeability or hydraulic conductivity, varies with direction. A geologic unit is *heterogeneous* if the hydraulic properties vary spatially (i.e., they are dependent on position within the geologic unit). Hydraulic properties, such as hydraulic conductivity, usually vary spatially within a geologic unit, and they also may vary directionally. Therefore, characterization of a ground-water system in support of an MNA evaluation should include assessment of the degree to which anisotropy and heterogeneity affect ground-water flow and contaminant transport.

Homsher *et al.* (1991) noted that 70 to 90 percent of data variability was caused by "natural", in-place variability (i.e., heterogeneity), with only 10 to 30 percent of variability being contributed by the rest of the data generation process (such as the sample collection procedures, sample handling, laboratory handling and cleanup, laboratory analyses, data handling, data reporting, and data interpretation).

As new technologies, such as DPT detection systems and passive diffusion bag samplers are applied to subsurface and aquifer characterization, marked vertical heterogeneities in contaminant concentrations are being found (e.g., Hurt *et al.*, 2001). The high degree of

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heterogeneity observed at some sites complicates interpretation of ground-water data because the proportion of mixing between water from more contaminated horizons with water from less contaminated horizons is an uncontrolled and unconsidered variable for the vast majority of monitoring well sampling plans. On the other hand, the ability to carefully delineate vertical heterogeneity in contaminant concentrations offers the opportunity to improve sampling designs (by focusing on discrete sampling locations) and to facilitate remediation treatment strategies (by focusing treatment applications) on specific ground-water horizons that may lead to cost and time savings through an increase sampling and treatment efficiency (Tillman and Sohl, 2001).

Vertical heterogeneity can be assessed by observing and describing the lithology encountered during advancement of boreholes for soil sampling and/or ground-water monitoring well installation purposes, and horizontal heterogeneity can be assessed by comparing boring logs from multiple locations. Detailed lithologic information also can be obtained via the use of CPT methods. Performance of aquifer slug tests in monitoring wells located throughout the site provides information on overall trends in spatial aquifer heterogeneity. If the scale of vertical heterogeneity is larger than monitoring well screen length, slug tests may be able to help identify and quantify preferential ground-water migration pathways. However, if the scale of vertical varation is smaller than the well screen length, slug tests are less likely to be helpful in identifying preferential flowpaths. Heterogeneity in lithology and spatial hydraulic conductivity information should be combined to support development of the CSM.

Perhaps the most common type of anisotropy encountered in consolidated or unconsolidated sediments is caused by horizontal layering, which causes the hydraulic conductivity in the horizontal directions (k_x and k_y) to be higher than that in the vertical direction (k_z). Freeze and Cherry (1979) state that, in the field, it is not uncommon for layered heterogeneity to lead to regional anisotropy ratios ($k_x:k_z$ or $k_y:k_z$) on the order of 100:1 or more. Understanding of the effects of anisotropy particularly important in geologic units exhibiting substantial secondary permeability and fracture flow (Section 3.4.2.5). Although quantification of k_x, k_y, and k_z is beyond the scope of many site characterization efforts, the stratigraphic controls on the vertical migration of contaminants should, at a mimimum, be qualitatively evaluated by characterizing the stratigraphy in the area of interest through borehole drilling using conventional or DPT methods.

3.4.2.5   Potential for Fracture Flow

In most instances, ground water is primarily found in the pore spaces between grains; this is termed primary porosity. However, the primary porosity of some sedimentary geologic units such as limestone, and of igneous and metamorphic rocks, is very low to non-existent because they are comprised of interlocking crystals. In these types of geologic units, ground water is present primarily in linear features such as joints, fractures, and bedding planes; these features are termed secondary porosity. Joints, fractures, and bedding planes in soluble rocks such as limestone can be enlarged over time as minerals dissolve into ground water that is percolating through the openings, resulting in significant flow systems that can transmit large volumes of water through discrete passageways.

Fracture-flow systems are characterized by a high degree of heterogeneity and anisotropy. In some cases, the geologic unit may be sufficiently fractured to act like an equivalent porous medium, at least on a more regional scale (i.e., the blocks of unfractured rock are analogous to the grains of a clastic sedimentary rock such as a sandstone). However, on a more local scale, ground-water flow and contaminant migration may be highly channeled such that it may be difficult to determine ground-water migration pathways and plume boundaries. In these cases, it

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may be desirable to define the dominant fracture patterns through fracture trace analysis using aerial photographs and/or perform tracer tests to define solute migration pathways. Highly-fractured zones (e.g., fault or shear zones) may be preferential pathways for ground-water flow. Alternatively, highly-fractured zones may contain abundant, highly-weathered and fine-grained gouge material that act as a barrier to ground-water flow. USEPA (1999a) states that MNA will not generally be appropriate where site complexities such as the presence of fractured-rock aquifers or karst systems preclude adequate monitoring.

3.4.3 Defining Relevant Contaminant and Geochemical Characteristics of the Ground-water System

During initial or supplemental site characterization activities, the nature, magnitude, and 3-D extent of dissolved hydrocarbons should be documented and quantitatively evaluated via grab sampling or the installation and sampling of temporary or permanent ground-water monitoring wells. These site characterization activities are necessary to evaluate plume dynamics (i.e., whether the contaminant plume is stable, expanding, or contracting over time). Establishing the nature and extent of contamination and plume dynamics is important for identifying 1) current or potential future risks to human health and the environment and 2) whether additional source reduction activities are needed to produce plume stability or expedite the rate at which the plume is diminishing in terms of extent and/or concentration.

Since the publication of the original protocol (AFCEE, 1995), a large body of research and field evidence has demonstrated the nearly ubiquitous occurrence of biodegradation of BTEX, naphthalene, and various other fuel hydrocarbons under a wide variety of geographic, climatic, hydrogeologic, and geochemical conditions, by native microbial consortia (e.g., Buscheck *et al*., 1996; Mace *et al*., 1997; Rice *et al*., 1995; Parsons, 1999; Suarez and Rifai, 1999; Wiedemeier *et al*., 1999). The presence of anthropogenic carbon (e.g., fuel hydrocarbons) in the subsurface, either as a LNAPL or as dissolved constituents delivered via infiltration, will affect soil and ground-water chemistry in measurable ways, even in the absence of biodegradation activity. The literature is replete with examples of field measurements that show the formation of measurable and predictable changes in ground-water chemistry that are caused by biodegradation of fuel hydrocarbons though a series of sequential, microbially-mediated electron acceptor processes, as shown schematically on Figure 3.1 (e.g., Cozzarelli *et al*., 1990; Wilson *et al*., 1990; Lyngkilde *et al*., 1991; Bouwer, 1992; Vroblesky and Chapelle, 1994; Wiedemeier *et al*., 1999). By measuring the various contaminant concentrations and natural attenuation indicator parameters described in Section 3.4.3.4, the effects of MNA on fuel-related COCs in ground water can be documented and quantitatively evaluated for a site.

The following subsections briefly describe the installation of temporary and permanent monitoring wells for ground-water sampling, recommended TAL, and associated sampling procedures and analytical methods in the event that existing site characterization data is not sufficient to support an MNA evaluation. Additional details regarding well installation techniques, as well as recommended well development, ground-water sampling, and QA/QC procedures are provided in Sections D.2 and D.3 of Appendix D of this document and in the AFCEE *Model Field Sampling Plan, Version 1.1* (AFCEE, 1997b). Note that the procedures described in this document may require modification on a site-specific basis to comply with local, state, and federal regulations. Target analytes have been divided into three main categories: fuel-related COCs, indicators of redox condition, and supplemental indicators of geochemical conditions.

3.4.3.1   Monitoring Well Installation

Ground-water sampling is conducted to determine the concentration and distribution of contaminants and ground-water geochemical parameters. Ground-water samples may be obtained from temporary or permanent monitoring wells, or point-source sampling devices such as a Geoprobe®, Hydropunch®, CPT, Simulprobe®, BAT Enviroprobe®, or Waterloo Profiler®. Information about these and other types of grab-sampling devices is available on the internet by searching for these keywords.

Historically, temporary or permanent monitoring wells have been installed using a conventional drilling rig. The type of drilling rig selected for use (e.g., auger, air- or mud-rotary, cable-tool) was and is dependent on the target drilling depths and the types of subsurface materials expected to be encountered. More recently, use of DPT (e.g., Geoprobe®, Strataprobe®, CPT) to install small-diameter monitoring points has developed as a useful and cost-effective site-characterization method, and scientific support for the use of DPT is increasing (e.g., BP Corporation and USEPA Regions 4 and 5, 2002; AFCEE, 2004).

Advantages of DPT relative to conventional drilling primarily include lower cost and elimination of potentially contaminated soil cuttings requiring special handling and disposal. However, DPT cannot be used to penetrate bedrock, and difficulty may be experienced attempting to penetrate extremely stiff, cemented, and/or gravelly units. In addition, unless pre-sandpacked screens and bentonite seals are used (such as those available from Geoprobe®), installation of a sand filter pack and annular seals may be problematic due to the small diameter of the annular space between the well casing and the borehole wall.

Recent comparison of ground-water quality and hydraulic conductivity data from wells installed using DPT and conventional drilling methods (BP Corporation and USEPA Regions 4 and 5, 2002; Kram et al., 2001) indicated that water levels and concentrations of target analytes were similar between the two types of wells. However, the results of one study (BP Corporation and USEPA Regions 4 and 5, 2002), indicated a consistently lower hydraulic conductivity and higher total suspended solids concentrations in DPT wells (installed without a filter pack), which were attributed to poor well development.

Where subsurface conditions are favorable for use of DPT, use of this technique (with or without use of pre-packed screens and bentonite seals) to install temporary monitoring wells will facilitate rapid and relatively inexpensive plume definition and collection of sufficient data to allow a more thorough evaluation of site-specific heterogeneity and the subsurface distribution of contamination (see Section 3.4.2.4). Use of field analytical techniques that provide real-time data in conjunction with DPT would be consistent with the triad approach that USEPA's OSWER is promoting to more effectively and efficiently characterize, monitor, and clean up hazardous waste sites. This approach is based on using an integrated triad of systematic planning, dynamic work plans, and real-time measurement technologies to plan and implement data collection and technical decision making at hazardous waste sites (USEPA, 2001c).

Once the plume is adequately characterized, installation of a relatively small number of permanent monitoring wells at key locations using DPT or conventional drilling and well installation techniques should be performed to obtain definitive data and facilitate LTM. Note that state-specific regulations should be reviewed to confirm that use of DPT wells for LTM is acceptable. Monitoring well design, drilling, and installation techniques are discussed in more detail in Section D.2.2 of Appendix D.

Because fuel releases to ground water typically originate as LNAPL, and ground-water flow is laminar, fuel-related COCs are typically found in the shallow portions of the aquifer. As such, the recommended screen interval for monitoring fuel-related contaminants is across the water table. In general, USEPA recommends that the screened interval for monitoring wells should be 10 feet (or less), and that screen intervals not extend across multiple hydrostratigraphic units. In areas where large annual fluctuations in the ground-water surface elevation occurs (e.g., greater than 5 feet), longer screens may be required for monitoring at different times of year.

3.4.3.2 Monitoring Well Development

Prior to collection of ground-water samples to obtain definitive analytical data, newly-installed monitoring wells (or wells that have not been sampled for several years) should be developed as described in Section D.2.2.3 of Appendix D. The adequacy of well development should not be assessed solely based on stabilization of field water quality parameters (e.g., pH, conductivity, dissolved oxygen [DO]) or on removal of a pre-determined volume of water. Rather, the adequacy of development should be judged based on the turbidity of the extracted water, because achieving an acceptable degree of water clarity is the primary objective of development. In most cases, the well will be developed more effectively using a combination of surging and ground-water extraction than by ground-water extraction alone.

3.4.3.3 Ground-Water Sampling

In general, the overall goal of any ground-water sampling program is to collect representative water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. MNA-related ground-water sampling at a fuel-release site can be performed using either a low-flow (i.e., "micropurge") method or a well-volume method (i.e., removal of a pre-determined amount of water such as a minimum of three casing volumes). Accurate measurement of redox-sensitive parameters during well purging will be facilitated by a low purge rate and minimal disturbance of the sample (USEPA, 1996c). Ground-water sampling procedures are discussed further in Section D.2.3 of Appendix D.

3.4.3.4 Ground-Water Analytical Protocol

The focus of this section is to describe the rationale and collection techniques for the parameters necessary to document MNA of fuel hydrocarbons that are dissolved in ground water, including aerobic and anaerobic biodegradation. Sorption effects on ground-water quality are not explicitly described in this section, as this topic was discussed in Section 3.4.2.3. Data obtained from the analysis of ground-water samples for the recommended analytes are used to document MNA of fuel-related contaminants, and also can be used as data input for either interpretive or predictive solute fate and transport models, when required. The following text describes each ground-water analytical parameter and the significance of each analyte in the MNA demonstration. Measurement of MNA parameters for mobile LNAPL, soil, and soil vapor is discussed in Section 3.3.

3.4.3.4.1 Frequency of Parameter Measurement during Site Characterization

MNA-related ground-water sampling activities conducted at a fuel-contaminated site can be grouped into four phases including:

1. Initial site characterization,
2. Baseline or validation monitoring,
3. Long-term monitoring, and

4. Periodic remedy evaluation.

During Phase 1 (initial site characterization), a more-comprehensive set of contaminants of potential concern (COPCs), geochemical natural attenuation indicator parameters, and hydrogeologic data (e.g., water levels, hydraulic conductivity) are measured to define site chemical/geochemical and hydrogeologic conditions (**Table 3.3**). During Phase 2 (baseline/validation monitoring), the conditions identified during Phase 1 are confirmed, and temporal (e.g., seasonal) variability in these conditions is assessed. The comprehensive list of geochemical indicator parameters targeted for analysis during Phase 1 is retained for Phase 2 monitoring; however, the list of COPCs targeted for analysis may be shortened for Phase 2 as contaminants of actual concern are identified from the Phase 1 results. For example, if the nature of the release is not known with certainty, then VOCs, SVOCs, GRO, and DRO may be targeted for analysis during Phase 1. The resulting data can then be used to identify those analytes that exceed regulatory criteria and/or pose a potential risk to human health or the environment. In addition, the temporal variability in hydraulic gradients and ground-water flow directions should be evaluated during Phase 2 via continued water-level measurement. It is recommended that Phase 2 monitoring be performed on a quarterly basis for a minimum of one year to evaluate seasonal variation in ground-water hydraulics, contaminant concentrations, and (as appropriate) ground-water redox indicator and other water-quality indicator parameters.

Typically, the TAL and monitoring frequency will be reduced during Phase 3 (LTM). The TAL and monitoring frequency will be dependent upon site-specific factors, and may be modified over time as new information is obtained. However, at a minimum, the TAL should include COCs, DO, oxidation-reduction potential (ORP), temperature, pH, conductance, and turbidity (Table 3.3). Optimization of Phase 3 LTM programs in terms of numbers and locations of wells sampled and sampling frequency is discussed in Section 5.

For Phase 4 (periodic remedy evaluation), a more-complete TAL, similar to that used during Phase 2, should be employed to facilitate a comprehensive assessment of site conditions and remedial progress. Phase 4 monitoring should be performed relatively infrequently (e.g., every five years) to support CERCLA 5-year reviews, OPS determinations, or other applicable regulatory requirements.

3.4.3.4.2   Fuel-derived Contaminants

Sampling and analysis for fuel-related compounds is required during the site characterization phase to demonstrate the nature and extent of contamination, and during the MNA assessment phase to demonstrate the nature of plume dynamics (e.g., stabilized, expanding, receding plume over time). Various types of analytical procedures can be used to determine the type, concentration, and distribution of fuel hydrocarbons in the aquifer system for the purpose of meeting site-specific DQOs. As described in Section 1.4, the most common COCs at fuel-release sites include BTEX, PAHs, and, at gasoline sites in some states, fuel additives. The following sections provide discussion of sample collection and analysis for the most common classes of fuel-related contaminants found in ground water. **Table 3.4** provides a summary of the analytical methods, potential data uses, and data quality concerns when performing analysis for fuel-related contaminants. Additional discussion of ground-water sampling and analysis for fuel-related contaminants is provided in Section D.2 of Appendix D.

VOCs in Ground Water

Volatile organic hydrocarbons (e.g., BTEX and MtBE, when present) are of primary interest to regulatory agencies due to toxicity concerns and the relatively high mobility of these

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TABLE 3.3
PHASED APPROACH TO SITE MONITORING

Sample Medium and Recommended Analytes	Initial Site Characterization	Validation/Baseline Monitoring	Long Term Monitoring	Periodic Remedy Evaluation
Residual LNAPL and Soil				
Contaminants of Potential Concern[a]	X			
Contaminants of Actual Concern[b]				*[c]
Total Organic Carbon	X			
Bioavailable Iron	X			*[c]
Mobile LNAPL				
Contaminants of Potential Concern[a]	X			
Contaminants of Actual Concern[b]		X		X
Soil Vapor				
Volatile Contaminants of Potential Concern[a][g]	X			
Volatile Contaminants of Actual Concern[b][g]		X	X	X
Methane	X			X
Carbon Dioxide	X			X
Dissolved Constituents (Ground Water)				
Contaminants of Potential Concern[a]	X			
Contaminants of Actual Concern[b]		X	X	X
Total Organic Carbon	X			X
pH, Specific Conductance, Temperature, Turbidity[d]	X	X	X	X
Dissolved Oxygen[e]	X	X	X	X
Nitrate	X	X		X
Ferrous Iron	X	X		X
Sulfate	X	X		X
Methane	X	X		X
Oxidation/Reduction Potential[e]	X	X	X	X
Alkalinity	X	X		X
Other Indicators[f]		*		*

[a] Contaminants of Potential Concern (COPCs) are identified based on all available information concerning the nature of the release, and may include total petroleum hydrocarbons.

[b] Contaminants of Actual Concern may consist of a subset of the COPCs, depending on the results of the initial site characterization.

[c] * = optional analysis.

[d] Recommended field measurements used to document water quality stabilization when using low-flow sampling techniques.

[e] Optional field measurements used to document water quality stabilization when using low-flow sampling techniques.

[f] "Other Indicators" of groundwater quality may include carbon dioxide, dissolved hydrogen, microbial acids (PLFAs/VFAs), and hydrogen sulfide. Collection and analysis of these parameters at fuel-release sites should be limited to specific instances where there is a demonstrated need for these data.

[g] Target for analysis if vapor intrusion into structures potentially poses a health-risk or explosion hazard. Soil vapor analysis also can be used to preliminarily identify zones of soil and/or ground-water contamination.

TABLE 3.4 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING COMMON CONTAMINANTS OF CONCERN IN GROUND-WATER AT FUEL-RELEASE SITES [a/]

Analysis	Method Description [Designation]	Comments	Data Use	Potential Data Quality Concerns
Petroleum Hydrocarbons				
Aromatic hydrocarbons (e.g., BTEX, TMB isomers, MtBE [optional])	Fixed-base GC/MS method [SW8260B] [b/] or fixed-base GC method (SW8021B)	Analysis may be extended to higher molecular weight alkyl benzenes.	• BTEX compounds are primary target analytes for MNA assessment of ground-water plume stability; • Measurement of BTEX concentrations required for regulatory compliance; and • TMBs can potentially be used to monitor plume dilution if degradation is primarily anaerobic.	• Volatiles lost during sample collection and/or shipment • VOC biodegradation due to improper preservation.
Polycyclic aromatic hydrocarbons (PAHs)	Fixed-base GC/MS method [SW8270C] or HPLC method [SW8310]	Analysis needed only when required for regulatory compliance.	• Measurement of one or more PAH concentrations may be required for regulatory compliance.	• Semi-volatiles lost during shipment and/or biodegradation due to improper preservation.
TPH (e.g., TRPH, GRO, DRO) [c/]	Fixed-base method will vary by required analysis	Compliance requirements for TPH vary by regulatory agency. Refer to (Appendix B) for additional detail.	• Monitor the reduction in concentrations of total fuel hydrocarbons (in addition to BTEX) due to natural attenuation; and • Infer presence of an emulsion or surface layer of petroleum in water sample, as a result of sampling.	• Volatiles lost during sample collection and/or shipment • VOC biodegradation due to improper preservation.
Inorganic Constituents				
Arsenic (optional)	Fixed-based various methods available (see E200)[d/]	Perform only if required by regulatory agency; Recommendation intended for locations where arsenic minerals are found in native soils/bedrock.	• Determination if anaerobic biological activity is solubilizing arsenic from native aquifer materials.	• Improper acidification prior to analysis may lead to errors in sample measurement.

[a/] Analyses other than those listed in this table may be required for regulatory compliance.

[b/] "SW" refers to *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods, SW-846, 5th revision* (USEPA, 1998c).

[c/] Total petroleum hydrocarbon (TPH) does not, by itself, define a standard test, but rather the hydrocarbons found within the boiling range defined by a specific test. Several common TPH ranges include: Total Recoverable Petroleum Hydrocarbons (TRPH), corresponding to compounds that are extracted using method-specific solvent(s); Gasoline Range Organics (GRO), corresponding to the range of alkanes from C_6 to C_{10}; Diesel Range Organics (DRO), corresponding to the range of alkanes from C_{10} to C_{28}. Other methods (USEPA or state-specific) are available, and it is recommended that users of this protocol review state-specific and site-specific data requirements when collecting TPH data.

[d/] "E" refers to *Methods for Chemical Analysis of Water and Wastes* (USEPA, 1983).

NOTE: BTEX = benzene, toluene, ethylbenzene, and xylene isomers; TMB = trimethylbenzene; MtBE = methyl ter-butyl ether; TPH = total petroleum hydrocarbons, TRPH = total recoverable petroleum hydrocarbons; VOC = volatile organic compound; GC/MS = gas chromatography/mass spectrometry; HPLC = high-pressure liquid chromatography.

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compounds. Substantial concentrations of BTEX compounds are present in most gasoline and historical jet-fuel releases. Due to the relatively high solubility of the BTEX compounds, and the fact that ground-water quality standards for one or more of the BTEX compounds exist in all 50 states, measurement and evaluation of historical changes in BTEX concentrations over time and space has become common practice for determining if the dissolved portion of a fuel-related contaminant plume is stable, expanding, or receding. At gasoline stations located in states where MtBE has been classified as a regulated compound and its use is known or expected, analysis for MtBE may be required.

In addition to BTEX and MtBE, dissolved concentrations of tetramethylbenzenes (TeMBs) and trimethylbenzenes (TMBs) are also of interest when evaluating MNA at fuel-release sites, as these compounds can be used, in some instances, as 'tracers' of fuel-related contaminant migration. Use of conservative tracers to calculate biodegradation rates is discussed in detail in Appendix C.3.3 of the original protocol (AFCEE, 1995). This text also provides an example calculation of how the tracer method can be applied to fuel-release sites. TeMB and TMBs have been considered tracers in the anaerobic portion of fuel-related plumes because these compounds are believed to be relatively recalcitrant to degradation under the anaerobic conditions that typically develop in the vicinity of fuel releases. In addition to interest as a tracer, several states have promulgated regulatory standards for TMBs, which would require assessment of these compounds as part of the overall site remedial strategy.

Based on these considerations, it is recommended that the volatile organic hydrocarbon analysis for fuel-release sites (USEPA Method SW8260B) include BTEX, TeMB, TMBs, and, when required, MtBE. Due to the volatile nature of these compounds, the use of low-flow sampling techniques has become more common, although use of the well-volume approach described in Section 3.4.3.3 in combination with higher flow rate pumping, bailing, or foot-valve techniques is still generally allowed. Previous research has indicated that the combined dissolved concentrations of BTEX and TMBs should not be greater than about 30 mg/L for a JP-4 spill (Smith *et al.*, 1981) and approximately 135 mg/L for a gasoline spill (Cline *et al.*, 1991; API, 1985). If these compounds are present at a combined concentration greater than 30 mg/L (JP-4 site) or 135 mg/L (gasoline site), sampling errors such as emulsification of LNAPL in the ground-water sample may have occurred.

Note that recent changes in the composition and type of fuels that are currently being used at USAF bases may produce noticeable changes in the way sites are evaluated over time. For example, the replacement of JP-4 with JP-8 jet fuel will cause BTEX and other relatively soluble (and volatile) compounds to become less common at future jet-fuel release sites. In addition, a potential ban on the use of MtBE as a fuel oxygenate would likely lead to the use of other fuel oxygenates (e.g., ethanol, *tert*-butyl alcohol [TBA], *tert*-amyl methyl ether [TAME]) that may be regulated compounds themselves or, in the case of ethanol, affect BTEX plume dynamics inways that have not been well-defined. In this scenario, analysis of additional VOCs may be required to demonstrate regulatory compliance and implement a site exit strategy.

SVOCs in Ground Water

PAHs are the primary SVOCs that are regulated in ground water at fuel-release sites. Naphthalene is the most soluble PAH, and is therefore the most likely PAH to be detected in ground water. At least 25 states currently have regulatory standards for at least one PAH compound, and three states are currently requiring a comprehensive analysis for SVOCs in ground water at fuel-release sites. Table 3.4 lists the two analytical methods that are most commonly used for PAH analysis, some potential uses of PAH data, and a list of data quality

concerns that should be considered when collecting and evaluating PAH concentration data. Determination of whether SVOCs are required for analysis in ground water and, if so, the preferred method of analysis, should be based on state and local requirements for these compounds. For example, use of USEPA Method SW8310 (which has lower method detection limits [MDLs] than USEPA Method SW8270) may be necessary at some sites to detect low concentrations of PAHs and facilitate comparison to regulatory standards or guidance.

TPH in Ground Water

More than half of the state regulatory agencies currently are requiring analysis for entire classes of petroleum hydrocarbons in soil or ground water (see Appendix B for additional details). Given the variation in requirements and methods for assessing TPH at fuel-release sites, users of this protocol are encouraged to review state- and site-specific data requirements when collecting TPH data with the objective of ensuring that the type of sample collection and analysis performed is consistent with the requirements of the regulatory agency(ies) charged with oversight of site remediation and closure.
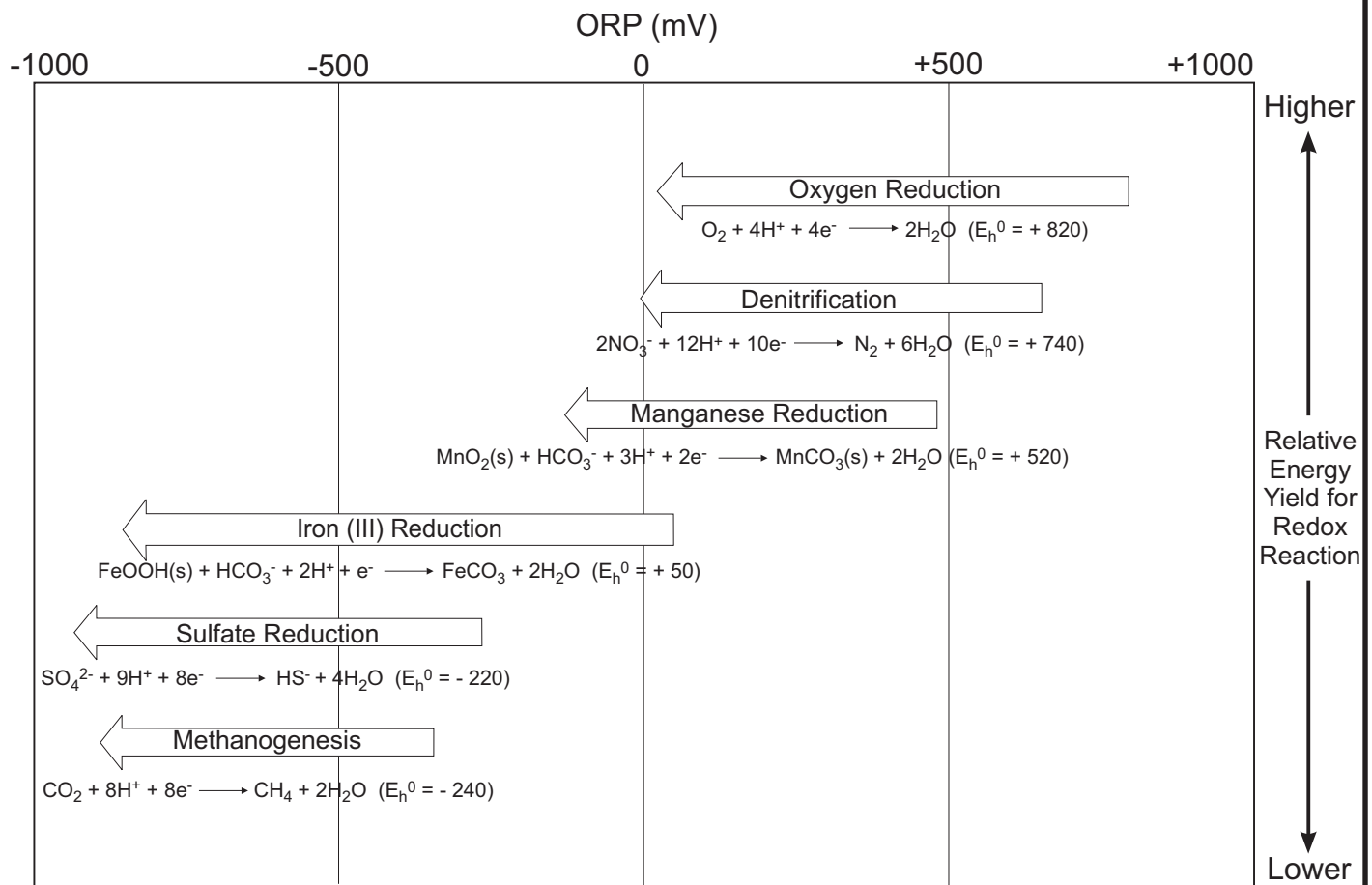
3.4.3.4.3   Electron Acceptors and Reaction Byproducts

Introduction of organic compounds released to the subsurface brings about measurable changes in the chemistry of ground water in and hydraulically downgradient of the release area. Biodegradation of organic compounds (including petroleum hydrocarbons) generally occurs via a series of sequential electron acceptor processes that can result in the depletion of specific electron acceptors and the generation of specific reaction byproducts. In the subsurface environment, the typical sequence of electron acceptor utilization proceeds from oxidizing conditions to increasingly more reduced conditions (as shown on **Figure 3.3**) in the order of oxygen-reduction (highest energy yield) through nitrate-reduction, manganese-reduction, ferric-iron-reduction, sulfate-reduction, and finally to carbon dioxide reduction (i.e., methanogenesis, which is the lowest energy yield). Note that the utilization of a particular electron acceptor is likely to vary over time and space, as the system is thermodynamically driven toward equilibrium, and that one or more biodegradation processes may be active concurrently in a given location (e.g., Lyngkilde *et al.*, 1991; Baedecker *et al.*, 1993; Vroblesky and Chapelle, 1994; Borden *et al.*, 1995).

Measurement of specific electron acceptor and reaction byproduct concentrations over space and time provides data that can be used to evaluate the type and degree of contaminant degradation at a site; this is the second line of evidence used during an MNA evaluation (see Section 1.2). For example, concentrations of these constituents can be used as data input for fate and transport models that calculate petroleum hydrocarbon consumption due to aerobic and anaerobic biodegradation processes using a mass balance approach.

The recommended TAL for electron acceptors and reaction byproducts at fuel-release sites includes three aqueous electron acceptors (DO, nitrate, and sulfate) and two aqueous reaction byproducts (ferrous iron and methane). In addition, analysis for several other indicators of ground-water quality also is recommended, as presented in Section 3.4.3.4.4. The methods, data use, and potential data quality issues for these recommended parameters are discussed below and summarized in **Table 3.5**. Additional parameters that can be measured to describe ground-water quality (including additional electron acceptors and reaction byproducts that are not discussed in this section) but are not generally recommended as necessary for MNA evaluations at fuel-release sites are discussed at the end of Section 3.4.3.4.4.

FIGURE 3.3

SEQUENCE OF MICROBIALLY
MEDIATED REDOX PROCESSES

ORP (mV)

-1000   -500   0   +500   +1000

Higher ↑

Oxygen Reduction
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $(E_h^0 = + 820)$

Denitrification
$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$ $(E_h^0 = + 740)$

Manganese Reduction
$MnO_2(s) + HCO_3^- + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_2O$ $(E_h^0 = + 520)$

Iron (III) Reduction
$FeOOH(s) + HCO_3^- + 2H^+ + e^- \longrightarrow FeCO_3 + 2H_2O$ $(E_h^0 = + 50)$

Sulfate Reduction
$SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ $(E_h^0 = - 220)$

Methanogenesis
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$ $(E_h^0 = - 240)$

Relative Energy Yield for Redox Reaction

Lower ↓

Notes

ORP = Oxidation/Reduction Potential = E_h^0

1. These redox processes occur in order of their energy-yielding potential (provided microorganisms are available to mediate a specific reaction). Reduction of a highly oxidized species decreases ORP of the system.

2. The ORP of the system determines which electron acceptors are available for oxidation of organic carbon.

3. Redox sequence is paralleled by an ecological succession of biological mediators.

Adapted from Stumm and Morgan, 1995 and Norris *et al*., 1994.

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TABLE 3.5 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING GROUND-WATER REDOX CONDITION AND GEOCHEMICAL PROPERTIES AT FUEL-RELEASE SITES [a/]

Analysis	Method Description [Designation]	Comments	Data Use	Potential Data Quality Concerns
Indicators of Biological and/or Redox Condition				
Alkalinity	Field titration method using drop count [e.g., Hach AL-AP-MG/L] or digital titrator [e.g., Hach[b/] 8203];	Phenolphthalein method; Can also be performed using fixed-base laboratory method E310.	• General water quality parameter used as indicator to verify that site samples are obtained from the same ground-water system; • Provides estimate for buffering capacity of local ground-water; and • Increases in alkalinity measurements within the contaminant plume, relative to background, are also an indicator of biological activity.	• Analyze sample within 1 hour of collection (preferred), or preserve at 4°C for analysis within 24 hours.
Dissolved oxygen (DO) [c/]	Field probe with direct-read meter [E360.1 [d/]; A422F [e/]]		• Concentrations less than 0.5 mg/L generally indicate anaerobic degradation activity; • Data input for models that explicitly account for oxygen utilization as part of aerobic biodegradation calculations; and • Provides quantification of ground-water quality stabilization during low-flow sampling (and purging, if applicable).	• Introduction of atmospheric oxygen during sample collection and analysis; • Bubbles behind, or fouling of, probe membrane; • Improperly calibrated instrument.
Iron(II) (Fe^{2+})	Field Colorimetric method [Hach 8146]	Filter if turbid [f/]; Also referred to as Ferrous Iron	• Indicator of reduced conditions that may be conducive to anaerobic degradation processes that follow the depletion of oxygen, nitrate, and manganese; and • Can be used for calibration of models that include iron(II) production as part of iron(III)-based biodegradation calculations.	• Minimize exposure to atmosphere and perform sample analysis immediately to limit oxidation of iron(II) to iron(III); • Keep sample out of sunlight; • Potential turbidity interference for colorimetric test (must filter if turbid) [f/].
Methane (CH_4)	Fixed-base method [g/] [Kampbell *et al.*, 1989; SW3810[h/] Modified]	Method, as published by USEPA research lab, also provides quantification of ethene and ethane.	• Presence of methane suggests anaerobic degradation via methanogenesis; • Can be used for calibration of models that include methane production as part of methanogenic biodegradation calculations; and • Ethane and ethene data not used as part of fuel-related constituent degradation analysis.	• Dissolved gas loss during sample collection and/or shipment; • Improper preservation may allow biodegradation to affect methane concentration.
Nitrate (NO_3^-)	Fixed-base IC method [E300]		• Nitrate concentrations below detection suggest reduced redox condition when DO concentrations are less than 0.5 mg/L; and • Data input for models that explicitly account for nitrate utilization during anaerobic biodegradation calculations.	• Improper sample preservation.

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TABLE 3.5 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING GROUND-WATER REDOX CONDITION AND GEOCHEMICAL PROPERTIES AT FUEL-RELEASE SITES (Continued) [a]

Analysis	Method Description [Designation]	Comments	Data Use	Potential Data Quality Concerns
Indicators of Biological and/or Redox Condition (Concluded)				
Oxidation-reduction potential (ORP) [c]	Field probe with direct-read meter [A2580B]	ORP of ground-water influences, and is influenced by, local biodegradation processes; Parameter may range from more than 800 mV to less than -400 mV.	• Quantitative indication of the localized nature of biologically-mediated degradation of contaminants; and • Provides quantification of ground-water quality stabilization during low-flow sampling (and purging, if applicable).	• Minimize exposure to atmosphere and perform sample analysis immediately using flow-through or overflow cell.
pH [c]	Field probe with direct-read meter		• Indication of whether pH-sensitive processes (e.g., biodegradation) are being impacted by local ground-water condition; • When used in conjunction with alkalinity, may provide early indication that MNA processes are changing (e.g., transition from methanogenic to acetogenic conditions); and • Provides quantification of ground-water quality stabilization during well purging and low-flow sampling.	• Improperly calibrated instrument.
Sulfate (SO_4^{2-})	Fixed-base IC method [E300]	Although field methods exist, these methods are not recommended based on cost considerations and potential for turbidity interference.	• Sulfate concentrations within the plume that are less than background may indicate biodegradation due to sulfate-reduction; and • Data input for models that that explicitly account for sulfate utilization during anaerobic biodegradation calculations.	• Sample not stored at 4°C.
Temperature [c]	Field probe with direct-read meter		• Provides quantification of ground-water quality stabilization during well purging and low-flow sampling; and • Qualitative indication that biodegradation processes may be slowed or enhanced due to impact of temperature on biodegradation rate (e.g., "Q10 rule").	• Improperly calibrated instrument; • Time sensitive; keep probe out of direct sunlight; shelter measurement location when extreme ambient conditions are present.

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TABLE 3.5 SUMMARY OF RECOMMENDED ANALYTICAL METHODS FOR EVALUATING GROUND-WATER REDOX CONDITION AND GEOCHEMICAL PROPERTIES AT FUEL-RELEASE SITES (Concluded) [a/]

Analysis	Method Description [Designation]	Comments	Data Use	Potential Data Quality Concerns
Indicators Used for Quantifying Ground-water Quality Stabilization [c/]				
Conductivity [c/]	Field probe with direct-read meter [E120.1/SW9050]		• General water quality parameter used as indicator to verify that site samples are obtained from the same ground-water system; • Provides quantification of ground-water quality stabilization during well purging and low-flow sampling.	• Improperly calibrated instrument.
Turbidity [c/]	Field turbidity meter [E1801.1; A2130B]	Readings based on nephelometric principle of turbidity measurement; Direct-read meters are also available.	• Provides quantification of ground-water quality stabilization during well purging and low-flow sampling; • Indicates when sample filtration is may be required for needed for colorimetric field tests.	• Improperly calibrated instrument; • Direct-read meters found on combination probes may become fouled with highly turbid water during purging. Collection of water samples in vials and measurement using a stand-alone turbidity meter (e.g., Hach Model 2100P) is recommended as a more robust measurement technique.

NOTES:

[a/] Analyses other than those listed in this table may be required to demonstrate regulatory compliance.

[b/] "Hach" refers to the Hach Company. Additional method description is provided in the *Hach DR/890 Colorimeter Procedures Manual, 5th Edition* (Hach, 2002) and the *HACH Digital Titrator Manual, Model 16900, Revision 4* (Hach, 2000), as applicable.

[c/] Parameters used to establish ground-water quality stabilization during well development commonly include pH, specific conductance, temperature, and turbidity. Parameters used to establish ground-water quality stabilization prior to ground-water sampling commonly include the aforementioned parameters plus DO and ORP.

[d/] "E" refers to *Methods for Chemical Analysis of Water and Wastes* (USEPA, 1983).

[e/] "A" refers to *Standard Methods for the Examination of Water and Wastewater*, *20th Edition* (American Public Health Association *et al.,* 1998).

[f/] Filter if the sample blank (i.e. ground-water sample that has not had an addition of method reagents) yields a measurement that is above the minimum limit of quantification for the parameter being measured. For ferrous iron, a typical limit of quantification is 0.5 mg/L, unless otherwise specified by site-specific DQOs.

[g/] Method commonly referred to as M/E/E (methane/ethane/ethene).

[h/] "SW" refers to *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods, SW-846, 5th revision* (USEPA, 1998c).

NOTE: IC = Ion chromatography.

Dissolved Oxygen

DO is the most thermodynamically favored electron acceptor used in the biodegradation of fuel hydrocarbons. DO concentrations are used to estimate the mass of contaminant that can be biodegraded by aerobic processes. In the field, decreased DO concentrations within an area impacted by petroleum hydrocarbons (relative to DO concentration measurements in a 'clean' background well) indicate that aerobic biodegradation is occurring or has previously occurred.

In areas where DO concentrations are greater than approximately 0.5 mg/L, anaerobic biodegradation of petroleum hydrocarbons by anaerobic bacterial activity is inhibited, and would not be expected to occur (Hutchins, 1991: Chang *et al*. 1993). Because DO concentrations will be affected by sample aeration, low-flow sampling techniques (as described in Section 3.4.3.3) with a direct-reading meter connected to a flow-through cell or other appropriate sampling device (e.g., 'overflow cell' using an Erlenmeyer flask that keeps the probe on the direct-read meter submerged) is the preferred method for measuring DO. If a sampling technique other than low-flow sampling is being used, precautions should be taken to prevent sample aeration, and data quality should be carefully evaluated prior to using DO measurements collected in this manner as part of an MNA evaluation.

Using conservative stoichiometric calculations that assume no biomass yield and complete mineralization of BTEX compounds to carbon dioxide and water, aerobic microbes are estimated to be able to degrade approximately 0.32 mg/L of BTEX for each 1.0 mg/L of DO that is consumed. The stoichiometry of BTEX biodegradation via aerobic respiration is described in Appendix A.

Nitrate

After DO has been depleted by microbiological activity in the affected area, nitrate is generally the next sequential electron acceptor that is consumed, in an anaerobic biodegradation process called denitrification. The oxidation of organic carbon during denitrification provides an energy yield to denitrifying microbial populations that is nearly as large as the energy provided by oxygen-reduction to aerobic microbial populations during aerobic biodegradation. In the field, decreased nitrate concentrations within the affected area, relative to background nitrate concentrations, suggest that biodegradation via denitrification is occurring or has previously occurred. At sites where background nitrate concentrations are low, nitrate-reduction will not be a significant contributor to the overall electron acceptor capacity.

Using the conservative stoichiometric relationship for BTEX degradation via denitrification (see Appendix A) that assumes no biomass yield and complete mineralization, each 1.0 mg/L of ionic nitrate consumed by microbes is predicted to result in the destruction of approximately 0.21 mg/L of BTEX.

Iron

In most pristine, shallow, unconfined aquifer systems, ground-water geochemical conditions are commonly pH neutral and aerobic. Under these conditions, the dominant iron species is found as solid phase ferric iron (iron[III]; Fe^{3+}) minerals, and little or no detectable concentrations of the more soluble, reduced species, ferrous iron (iron[II]; Fe^{2+}). Numerous researchers have shown that, upon release of fuel hydrocarbons to the subsurface, various petroleum hydrocarbon compounds may be anaerobically biodegraded through the reduction of the solid phase electron acceptor ferric iron (e.g., Anderson and Lovley, 1999; Lovley and Lonergan, 1990).

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The *Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) Protocol* (AFCEE 2000b) describes methods of sample collection and analysis for the direct measurement of bioavailable ferric iron in soil. To date, there has been limited data collection and reporting of bioavailable ferric iron at fuel-contaminated sites, due to a combination of the relatively recent development of the AMIBA protocol and to additional expense of mobilizing drilling equipment to a site for the collection of soil samples during each sampling event. In contrast, the measurement of dissolved ferrous iron, a byproduct of ferric iron reduction, has been analyzed at a large number of fuel-contaminated sites, as there is a relatively minor incremental cost incurred to perform this field analysis as part of periodic ground-water sampling events.

Due to the relatively low cost of ferrous iron analysis of ground-water samples, the collection and analysis of ferrous iron is recommended at sites where a second line of evidence (i.e., indirect geochemical evidence of the type of biodegradation) is required to support findings on plume stability (the first line of evidence). Pending development and publication of a study on the cost-effectiveness of applying the AMIBA protocol to fuel-contaminated sites, direct measurement of bioavailable iron analysis, as described in the AMIBA protocol, should be evaluated on a site-specific basis. At existing sites where the long-term stability of MNA is uncertain and/or the regulatory agency is requiring mass balance calculations that demonstrate that the assimilative capacity of the aquifer system is sufficient to support natural attenuation over the long term, application of the AMIBA protocol may be necessary to support the MNA option. At other sites, RPMs are advised to compare the benefits of a direct estimate for the mass of solid phase electron acceptor that is remaining in and downgradient of a fuel-hydrocarbon plume with the costs of collecting this additional data and the potential savings that may be realized due to accelerating site closure.

Using conservative stoichiometric calculations that assume no biomass yield and complete mineralization of BTEX compounds, ferric iron-reducing microbes are predicted to produce approximately 21.8 mg/L of ferrous iron for each 1 mg/L of BTEX that is biodegraded (see Appendix A). In the subsurface environment, ferrous iron readily reacts with dissolved anions (including sulfide, a product of sulfate reduction) to produce ferric iron precipitates which may or may not be in a bioavailable form. While detection of ferrous iron in ground-water samples collected at fuel-release sites is a strong indication that anaerobic conditions exist at a particular location, mass-balance calculations that use ferrous iron concentrations to predict the mass of biodegraded contaminant should be used with caution, as described in Section 4.2.2.2, due to the effects of ferrous iron precipitation. Also note that the federal SMCL for iron in drinking water is 0.30 mg/L due to color, taste, and staining issues, and that this standard may be applicable at some sites.

Sulfate

Sulfate also may be used as an electron acceptor during microbial degradation of natural or anthropogenic organic carbon under anaerobic conditions (Grbic-Galic, 1990; Coates *et al.*, 1996), in a process known as sulfate reduction. Sulfate reduction typically occurs after dissolved oxygen, nitrate, and at least some bioavailable ferric iron have been depleted in the microbiological treatment zone. In the field, decreased sulfate concentrations within the fuel-contaminated area, relative to background, indicates that anaerobic degradation via sulfate-reduction is or has occurred.

Using stoichiometric calculations that assume no biomass yield and complete mineralization of BTEX compounds to carbon dioxide and water, anaerobic biodegradation via sulfate reduction is predicted to result in the destruction of approximately 0.21 mg/L of BTEX for each

1.0 mg/L of sulfate consumed. The stoichiometry of BTEX biodegradation via sulfate reduction is described in Appendix A. It should be noted that the federal SMCL for sulfate in drinking water is 250 mg/L due to taste issues, and may be applicable at some sites.

Methane

Methanogenesis is an anaerobic biodegradation process where carbon dioxide (or acetate) serves as an electron acceptor and methane is produced as a reaction byproduct. Methanogenic biodegradation is inhibited by the presence of many other electron acceptors, and generally becomes the dominant terminal electron acceptor process only after oxygen, nitrate, bioavailable ferric iron, and sulfate have been depleted. The detection of methane in ground water is indicative of strongly reducing conditions. Because methane is not a constituent of fuels, the presence of methane in fuel-impacted ground water at concentrations that exceed background levels (which are commonly below detection limits in pristine, shallow aquifers) provides an indication of methanogenic degradation of fuel hydrocarbons.

Using conservative stoichiometric calculations that assume no biomass yield and complete mineralization of BTEX compounds to carbon dioxide and water, methanogenic biodegradation is predicted to result in the production of 0.78 mg/L of methane for every 1 mg/L of BTEX consumed (Appendix A).

3.4.3.4.4   Other Geochemical Indicators

In addition to the changes in electron acceptor and reaction product concentrations described above, biodegradation processes may also influence, or, be influenced by other parameters that can be measured to assess ground-water redox and/or biological conditions. Four of the parameters discussed in this section – ORP, alkalinity, pH, and temperature – can be used to directly assess ground-water conditions in terms of suitability for biological activity. Two other parameters – turbidity and conductivity – are discussed because these parameters, in conjunction with DO, ORP, and pH, are commonly measured as part of demonstrating stabilization of ground-water quality during well development and purging procedures. The final parameters described in this section include several "additional" ground-water quality parameters that could be measured to provide insight into fate and transport mechanisms that may affect MNA. Measurement of these additional parameters is generally not recommended as part of a standard MNA evaluation at most fuel-contaminated sites, as some of them are considered to be redundant or of otherwise limited value relative to the parameters described in Table 3.5.

Oxidation-Reduction Potential

ORP (or redox potential) of ground water is a measure of electron activity that indicates the relative tendency of a solution to accept or transfer electrons. Redox reactions in ground water contaminated with petroleum hydrocarbons are believed to be biologically mediated, and therefore, the ORP potential of a ground-water system depends upon and influences rates of biodegradation. Knowledge of the ORP of ground water also is important because some biological processes operate only within a prescribed range of redox conditions. The redox potential of ground water generally ranges from -400 millivolts (mV) to 800 mV. Figure 3.3 shows the typical range of ORP observed in ground water when various electron acceptor processes are active. As shown by the Gibbs free energy estimates that are provided with the electron acceptor half-reactions on this figure, the order of electron acceptor utilization on this figure is displayed in descending order with the highest energy yield reaction (oxygen reduction) on top and the lowest energy yield reaction (methanogenesis) on bottom. As is also shown on this figure, the ranges of ORP measurements for each electron acceptor process overlap,

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indicating that ORP measurements may not singularly define the dominant redox condition at a particular location. Rather, ORP measurements provide a general indication of redox condition that can be used in conjunction with the electron acceptor and reaction byproduct data described above to assist in identifying the dominant electron acceptor process at a particular location during MNA assessment.

Another potential use of ORP data is to provide a real-time indication of the location of the contaminant plume during initial site investigations, particularly if sufficient time has elapsed since the fuel release for highly-reducing, anaerobic conditions to predominate in an aquifer that would otherwise be oxidizing or only mildly reducing. Under these conditions, ORP measurements could be used during site investigations to determine the approximate extent of the contaminant plume by mapping locations where ORP is lower than background. In this case however, the potential for a low-ORP "shadow" to develop downgradient of the plume, as described by AFCEE (2000c) should be recognized.

When using ORP data in real-time or as an indicator of general ground-water quality, it is important to obtain at least one ORP measurement (and preferably more) upgradient of the plume and in the same stratigraphic unit (or units) as the measurements within the affected area. ORP measurements should be taken during well purging and immediately before sample acquisition using a direct-reading meter. Because ORP can be noticeably affected by sample aeration, low-flow sampling techniques (as described in Section 3.4.3.3) with a direct-reading meter connected to a flow-through cell or other appropriate sampling device is the preferred method for measuring ORP. If a sampling technique other than low-flow sampling is being used, precautions should be taken to prevent sample aeration, and data quality should be carefully evaluated prior to using ORP results as part of an MNA evaluation.

Alkalinity

Total alkalinity measurements of ground water provide a quantitative indication of the capacity of the ground-water system to neutralize acid. Alkalinity is defined as the net concentration of strong base in excess of strong acid with a pure carbon dioxide-water system as the point of reference (Domenico and Schwartz, 1997). Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, and potassium. These species result from the dissolution of rock (especially carbonate rocks), the transfer of carbon dioxide from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of ground-water pH because it buffers the ground-water system against acids generated during both aerobic and anaerobic biodegradation.

In general, areas contaminated by fuel hydrocarbons exhibit a total alkalinity that is higher than that seen in background areas. This observed increase in alkalinity is believed to occur because the microbially-mediated reactions that result in biodegradation of fuel hydrocarbons produce an increase in the total alkalinity in the system, as discussed in Appendix A. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and less pronounced during methanogenesis (Morel and Hering, 1993). In addition, Willey *et al.* (1975) show that short-chain aliphatic acid ions produced during biodegradation of fuel hydrocarbons can contribute to alkalinity in ground water.

pH

The presence and level of activity of microbial populations are affected by the pH of ground water; methanogenic bacteria are particularly sensitive to pH conditions. Microbes capable of degrading petroleum hydrocarbon compounds generally prefer environmental conditions where

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the pH is within the range of 6 to 8 standard units. The buffering capacity (as quantified by alkalinity measurements) of most aquifer systems is sufficient to maintain pH within this preferred range of conditions. Once the ambient pH range has been established during site characterization and subsequent monitoring at these well-buffered sites, the primary purpose of collecting pH data is to demonstrate ground-water quality stabilization during well development and purging prior to VOC sample collection. In aquifer systems where alkalinity is relatively low (e.g., less than about 30 mg/L as calcium carbonate [$CaCO_3$]), periodic measurements of pH upgradient from and within the contaminant plume should be recorded to determine if pH concentrations are decreasing over time and approaching acidic conditions that are less favorable for microbial activity. Monitoring for changes in microbial activity is important because a decrease in microbial activity has the potential to affect plume dynamics by changing the natural attenuation rate.

Because the pH of a ground-water sample can change significantly within a short time following sample acquisition, this parameter should be measured using a direct-reading meter connected to a flow-through cell or other appropriate technique, without filtration or preservation. Appendix D provides additional information on the use of pH for demonstrating ground-water quality stabilization during well development and purging.

Temperature, Conductivity, and Turbidity

Ground-water temperature, which typically ranges between 5 degrees centigrade (°C) and 25°C, directly affects both chemical solubility and the rate of microbial activity. As an example of temperature effects on solubility, a 10°C decrease in ground-water temperature (from 15°C to 5°C) would result in an approximately 22 percent increase in maximum DO solubility. In terms of microbial activity, a 10°C increase in temperature over the range between 5°C and 25°C would generally be expected to double the rate of hydrocarbon biodegradation (e.g., the "Q_{10}" rule). Ground-water temperatures less than about 5°C tend to inhibit biodegradation by slowing the rate of microbial activity. Recording ground-water temperatures during well purging is also recommended to demonstrate ground-water parameter stabilization prior to sample collection.

Conductivity (i.e., specific conductance, conductance) is a measure of the ability of a solution to conduct electricity (Radtke *et al.*, 1998). The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases. Recording conductivity measurements during well development and purging prior to sample collection is recommended as part of the procedure for demonstrating ground-water parameter stabilization, which in turn indicates that fresh water from the aquifer (as opposed to stagnant water stored in the well casing) is being purged. In addition, large variations in conductivities recorded in samples collected from different locations and/or depths may indicate that water at these monitoring points is coming from different hydrogeologic zones.

Because the temperature and conductivity of a ground-water sample can change significantly within a short time following sample acquisition, these parameters should be measured in unfiltered, unpreserved samples using a direct-reading meter connected to a flow-through cell or other appropriate sampling device. Alternatively, temperature can be measured using a thermometer inserted into the flow-through cell, as described in the original protocol (AFCEE, 1995).

Turbidity is a measure of the scattering effect that suspended solids have on light: the higher the intensity of scattered light, the higher the turbidity (Wilde and Gibs, 1998). Primary contributors to turbidity include clay, silt, finely-divided organic and inorganic matter, soluble colored organic compounds, and microscopic organisms (American Public Health Association *et*

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al., 1998). Turbidity is commonly measured in nephelometric turbidity units (NTUs), and cannot be correlated directly to a concentration measurement of suspended solids in ground water. In the field, turbidity measurements are used as part of the procedure for demonstrating ground-water quality stabilization during well development and purging prior to sample collection, and as an indicator of when samples may require filtration prior to colorimetric field measurements of analyte concentrations (e.g., ferrous iron).

Although many direct-reading ground-water quality meters also have the capability to measure turbidity, these probes can be unreliable or extremely slow to reach stabilization when measuring ground-water turbidity, particularly if the initial purging is highly turbid. One alternative that may yield more reliable results is to collect water samples in a clean, glass vial and measure for turbidity using a stand-alone portable turbidimeter unit (e.g., Hach Model 2100P).

Additional Parameters

In most cases, analyses for the primary MNA indicator parameters described above and listed in Table 3.5 are sufficient to document the occurrence and impact of natural attenuation processes on dissolved hydrocarbon contaminants. However, in instances where these primary indicator parameters are not internally consistent, or additional weight of evidence is necessary to document the occurrence of specific natural attenuation processes, the following additional geochemical or biological indicator parameters may provide additional evidence to support evaluation of an MNA-based remedy: chloride, manganese(II), hydrogen sulfide, dissolved hydrogen, carbon dioxide, volatile fatty acids (VFAs), and phospholipid fatty acids (PLFAs). Chloride concentration data can sometimes be used to help distinguish between ground water flowing from different sources or in different hydrostratigraphic units. The reaction endproducts manganese(II) and hydrogen sulfide can be used to provide site-specific evidence of manganese-reduction and sulfate-reduction, respectively. Analysis for dissolved hydrogen concentrations can be used to provide confirmatory evidence of the active electron acceptor process(es) at a particular site (e.g., Chapelle *et al*., 1996a). Measurements of carbon dioxide, VFAs and PFLAs can be used to document the increased the level of microbial activity that commonly occurs within dissolved hydrocarbon contaminant plumes. The decision to measure any or all of the above parameters should be based on a site-specific determination of whether each measured parameter can provide insight into active microbial processes and/or electron acceptor mass that can not be determined adequately from the primary indicator parameters.

The above list of parameters is not intended to encompass all possible parameters that can be (or are required by applicable regulations to be) measured at a particular site. For example, arsenic has been included on the list of additional parameters because naturally-occurring arsenic can be mobilized by the reducing conditions that normally follow anthropogenic carbon release into the subsurface. Considering that arsenic-bearing aquifer materials tend to be concentrated in specific regions, the decision to include arsenic in the list of monitored parameters should be based on knowledge of the presence or absence of arsenic-bearing minerals in the local or regional stratigraphy.

It is the authors' experience that measurement of the above 'additional' parameters is not required for the successful evaluation and documentation of MNA at most fuel-release sites. Therefore, measurement of the parameters described in this section is not recommended unless measurements of COCs and primary indicator parameters are unable to satisfy site-specific data needs or applicable regulatory requirements.

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3.4.3.5   Field versus Fixed-Base Laboratory Analysis of Ground-Water Quality Parameters

Technically sound and cost-effective ground-water analytical programs for MNA evaluations can be developed using field and/or fixed-base laboratory methods. For several of the parameters described above and listed in Table 3.5, both field and fixed-base laboratory analytical methods exist. Each type of test will likely have advantages and disadvantages in terms of cost, accuracy, MDL, skill requirements for field personnel, and time required for analysis. The decision on whether to perform parameter analysis in the field or in the laboratory should be based on the data collection objectives, experience and ability of the available sampling personnel, number of wells being sampled, range of parameters being measured in the field, and the analysis cost. The data collection objectives and the required accuracy of measurement should be specified as part of the DQOs for the site. For example, simple 'color-matching' colorimetric tests performed in the field may be suitable for screening-level analysis, but may not be sufficiently accurate to support more intensive and quantitative data analysis. Performing field analyses may require additional training for field personnel, and will almost always require additional time for completion of sampling and analysis at each well and/or additional on-site personnel to perform the analyses. In general, analytical testing in the field requires a relatively high initial investment in equipment and supplies, followed by a relatively low incremental cost for reagents used per test. Conversely, fixed-base laboratory analyses have little or no initial investment, but generally higher costs for each analytical test.

As an example, field and fixed-base laboratory analytical methods exist for nitrate, sulfate, and chloride. Although several of the field methods adequately quantify these parameters at a relatively low unit cost, experience has shown that fixed-based laboratory analysis by ion chromatography is generally a better approach for quantifying these parameters, in terms of both overall cost and analytical accuracy (e.g., USEPA, 2001c; API, 1997).

3.5   SURFACE-WATER CHARACTERIZATION

3.5.1   Ground-Water/Surface-Water Interactions

As part of the risk assessment and MNA evaluation process, it is important to determine if ground water is discharging to or being recharged by surface-water bodies that are currently impacted, or have the potential to be impacted in the future, by the dissolved contaminant plume. If ground water is determined to be discharging to a surface-water body, a potential exposure pathway may exist whereby fuel-related contaminants could come into contact with human and/or ecological receptors. In this scenario, contaminant concentrations in the surface-water body and/or in the ground-water plume should be measured to evaluate whether unacceptable exposure is occurring, or has the potential to occur in the future. Surface- and ground-water sampling techniques are described in Volume III of USEPA (1989) and Section 3.4 of this document, respectively. If current conditions are such that unacceptably elevated contaminant concentrations are present in a surface-water body, active remedies (e.g., *in situ* treatment, plume cutoff, source reduction) will be needed prior to implementation of an MNA remedy.

If surface water is found to be recharging ground water, the risk to potential receptors via a surface-water exposure pathway may not exist at a particular site. Surface water is generally aerobic and, if it recharges the ground-water system, may be a potential source of additional electron acceptors that can be used during biodegradation of fuel contaminants. At some sites, the recharge/discharge relationship may vary seasonally, resulting in enhanced bioremediation during periods of ground-water recharge.

If the nature of ground-water/surface-water interaction is unknown or uncertain, one method for evaluating whether ground water is recharged by or discharges to a surface-water body is to measure elevations of both the surface water and the water table adjacent to the surface-water body. For example, in situations where the elevation of the water table of an unconfined aquifer is below the water surface elevation of an adjacent surface-water body (e.g., a river or stream), water from the stream moves into the ground-water system, and the stream is known as a losing stream in that reach. In situations where the elevation of the water table is greater than the elevation of an adjacent stream, ground water discharges to the stream, which is known as a gaining stream (Freeze and Cherry, 1979). Surface-water elevations can be measured relative to locations on permanent structures in the water body (e.g., culvert inverts, bridge piers) or via installation of survey monuments.

Alternatively, the volumetric flow rate in a river or stream can be measured at several locations in the area of interest to determine whether it is gaining or losing. Use of this method will be most feasible and accurate in relatively small streams. Flow-rate measurement techniques are described in *Measurement and Computation of Streamflow* (United States Geological Survey [USGS], 1982).

A third method of determining whether a stream/river is gaining or losing is to install one or more simple temporary piezometers (e.g., open-ended steel pipes hand-driven at least 2 feet into the streambed) as described by the USGS (2002). If the stabilized water level inside the pipe is higher than the water level in the stream, then the hydraulic head in the ground-water system beneath the stream is higher than the head in the stream itself, and ground water is discharging to surface water.

3.5.2 Field Methods to Characterize Surface-water Contamination

Surface-water sampling methods will vary depending on the TAL and the size of the surface-water body. The reader is referred to ASTM (2002c) to determine the most appropriate method(s) for a particular site. When sampling for VOCs such as BTEX, a method that minimizes agitation and disturbance of the samples should be selected, and the samples should not be composited from multiple depths or areal locations to avoid loss of VOCs during the sampling process. Sample bottles containing acid preservative should not be submerged in the water to prevent loss of the preservative. In relatively large surface-water bodies (e.g., ponds, lakes, rivers, large streams), samples should be collected within the estimated plume discharge zone. For example, if a BTEX plume discharges to a large pond, the samples should be collected near the edge of the pond closest to the plume as opposed to in the middle of the pond or near the far bank.

If the site-specific DQOs include defining the dimensions of the plume discharge area and evaluating discharge "hotspots", then this can be accomplished using passive vapor diffusion samplers installed just beneath the bed of the surface water body. This technique is described in detail by the USGS (2002).

SECTION 4

RECOMMENDED METHODS FOR DESCRIBING AND EVALUATING MONITORED NATURAL ATTENUATION DATA

Following the collection of appropriate data to support an MNA evaluation (as described in Section 3), these data should be evaluated to determine if MNA, as either the sole remedy or as part of an engineered remedial approach, can be supported as protective of potential receptors, both at present and in the future. The text provided in this section presents the steps in this evaluation process, including a discussion on how to identify specific points of concern and decision criteria, refinement of the site CSM, spatial and temporal data analysis, and application of site-specific analytical or numerical models as necessary. Recommendations on data presentation methods for each evaluation technique are provided throughout this section, as the ability to convincingly and scientifically present findings of an MNA evaluation may be equally important as the evaluation itself when implementing the intended site exit strategy.

4.1   IDENTIFY SITE-SPECIFIC CONCERNS AND DECISION CRITERIA

As described in Section 2.3, the risk-based remediation methods most commonly applied to fuel-release sites rely on a clear understanding of current and future pathways that have the potential to lead to human or other environmental receptor exposure. When evaluating any remedy (MNA or otherwise), it is critical to identify physical features and the medium (e.g., soil, soil vapor, ground water, or surface water) that could serve to bring receptors into contact with COCs. Specific examples of physical features and media that could lead to exposure include:

- Buildings or other structures that are located in close proximity to a source of VOCs that could be carried in soil vapor to indoor air, thereby exposing site workers;

- Open excavations for utilities or structural foundations that could expose site workers to direct-contact with soil or inhalation of soil vapor;

- Water-supply wells (potable or non-potable) downgradient of a mobile dissolved contaminant plume that is expanding toward the wells; and

- Surface-water bodies that could serve as a discharge point for contaminated ground water.

Because these site-specific concerns are typically identified during the RI process, completion of this task may be as simple as reviewing existing reports. If the results of the RI are not available, the RI has not been completed, or it is suspected that there has been (or will be) a change in site use that was not considered in the RI, a site walk should be performed with the facility manager to determine how current or future land uses could result in exposure to potential receptors. Upon completion of this task, a base map showing relevant physical features should be obtained and annotated, as necessary, to display the location(s) of potential exposure receptors. This base map will also serve as the basis for illustrating the spatial relationship of fuel-release contaminated media to potential receptors.

In addition, most regulatory agencies will require that the responsible parties achieve numerical cleanup goals before final site closure can be granted. As described in Section 2.1.1, AFCEE (1999b), and ASTM (1995a), the RBCA process involves a tiered approach in which assessment and resultant remediation activities can be tailored to site-specific conditions and risks. For example, it is recommended that remediation targets for BTEX and PAHs in ground water be developed based on site-specific risk reduction objectives, rather than default use of drinking-water standards. For the purposes of an MNA evaluation, it is important to work with site regulators and other stakeholders to establish the specific compliance criteria for each affected medium (i.e., soil, soil vapor/indoor air, ground water, and surface water) that can be used for comparing results from data collection and/or model simulations with compliance criteria at specific monitoring locations. Using this type of systematic approach to determining specific contaminant concentration targets at specific compliance locations will provide a scientifically-defensible standard to evaluate protectiveness of the MNA alternative, as described in more detail in Section 5.3. For information on how risk-based, site-specific remedial objectives can be developed, users of this protocol are referred to the *Air Force Handbook for Remediation of Petroleum Contaminated Sites* (AFCEE, 1998) and *Streamlined Risk-Based Closure of Petroleum Contaminated Sites: Performance and Cost Results from Multiple Air Force Demonstration Sites* (AFCEE, 1999b).

4.2 DEVELOP CONCEPTUAL SITE MODEL FOR MNA EVALUATION

CSM refinement involves integrating newly gathered site characterization data to refine the preliminary CSM that was developed based on previously existing site data. During CSM refinement, all available site-specific data should be integrated to develop an accurate 3-D representation of the hydrogeologic and contaminant transport system over space and time. The refined CSM then can be used to determine which media will require data evaluation, how the results of this evaluation will be compared with site-specific remedial criteria, and as the basis for developing a site-specific contaminant fate and transport model, if required.

When developing and refining the CSM, it is important to recognize that some site characteristics will only vary with space, while others will vary with both time and space. For example, site geology can be considered to vary only with space. Site characteristics that are likely to vary over both space and time include contaminant concentrations, redox conditions, ground water flow directions, and water table elevations. The CSM should account for the fact that some of these variations may be seasonal (e.g., variation in ground-water flow direction or water table elevation), while others may follow specific events and continue to change over time (e.g., changes in contaminant concentrations and redox chemistry caused by fuel release and subsequent contaminant transport and natural attenuation).

Data representations that can be used to support development of a CSM for MNA evaluation at fuel-release sites include geologic logs, hydrogeologic cross-sections, potentiometric surface/water table maps, representations of spatial variation in contaminant and/or geochemical indicator parameters (e.g, isoconcentration contour [isopleth] maps, concentration-versus-distance plots), and representations of temporal variations in contaminant concentration data (e.g., concentration versus time plots, results of statistical analyses). The following discussion on data evaluation and representation is divided into:

- Physical site characteristics that control contaminant transport (Section 4.2.1); and

- Identification of chemical data trends for COCs and geochemical indicator parameters (Section 4.2.2).

The results of the evaluations described in Sections 4.2.1 and 4.2.2 can also be used to provide input data for various modeling tools that are discussed in Section 4.3. Additional information on the components and recommended procedures for developing a CSM for fuel-release sites is provided in Appendix C.

4.2.1   Site-specific Transport Effects

As described in Section 3.3.2 and shown schematically on Figure 3.1, fuels that are released to the subsurface as LNAPL will migrate vertically downward under the force of gravity until encountering either the water table or a layer of relatively low permeability (e.g., silt or clay layers). LNAPL can migrate across the water table and/or into low permeability layers; however the rate of vertical migration is slowed when the LNAPL encounters these subsurface features. To understand the nature of contaminant transport and distribution of contaminant between LNAPL, soil, soil vapor, and ground water, an understanding of the local geology near, and hydraulically downgradient of, the release is needed. The following text provides an approach for presenting geologic information collected using either conventional drilling or DPT methods.

4.2.1.1   Hydrogeologic Data Presentation

Geologic logs should be constructed that describe the aquifer matrix, including relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible fuel or fuel odor. It is also important to correlate the results of volatiles screening using soil sample headspace vapor analysis with depth intervals of geologic materials. The depth of lithologic contacts and/or significant textural changes should be recorded to the nearest 0.1 foot. This resolution is necessary because preferential flow and contaminant transport paths may be limited to thin stratigraphic units.

Using the geologic data recorded on the geologic logs, vertical cross-sections should be prepared with a focus on depicting changes in hydrogeological features laterally and vertically. A minimum of two hydrogeologic sections should be constructed; one parallel to ground-water flow and one perpendicular to the direction of ground-water flow. These sections should depict (to scale) the relationships between hydrostratigraphic units that underlie the site, including the location and areal distribution of transmissive and non-transmissive units. The location of the contaminant release and residual source area should also be shown. Hydraulic head data, including potentiometric surface (for confined aquifers) and/or water table (for unconfined aquifers) elevation data should be shown. These sections are useful in identifying potential preferential contaminant migration pathways and in serving as the basis for defining aquifer units when simulating contaminant transport using solute fate and transport models. In addition, cross-sectional base maps may be used to illustrate data trends or model predictions, particularly at sites where significant variation in contaminant transport with depth is observed.

4.2.1.2   Potentiometric Surface Maps

A potentiometric surface or water table map is a two-dimensional (2-D) graphic representation of equipotential lines shown in plan view. Data input for potentiometric maps includes well coordinates and the ground-water elevations measured at each well on-site. Because ground-water flows from areas of high hydraulic head to areas of low hydraulic head, such maps are used to evaluate the probable direction of plume migration and to estimate hydraulic gradients. These maps should be prepared using water levels measured in wells screened in the same relative position within the same hydrogeologic unit. Separate potentiometric maps should be developed for different horizons in the aquifer to document

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whether vertical variations in ground-water flow exist. To document seasonal variations in ground-water flow, separate potentiometric surface or water table maps should be prepared for quarterly water level measurements taken over a period of at least one year. In areas with LNAPL, the water level measured in a well screened across the water table will be lower than the actual water table elevation. To account for this effect, a correction must be made for the water table deflection caused by the LNAPL. Information on how to calculate this correction and prepare potentiometric surface map is discussed in Appendix C-2 of the original protocol (AFCEE, 1995).

4.2.1.3 Identification of Governing Solute Mass Transport Mechanisms

At sites where contaminants from the fuel release have reached ground water, it is important to quantify the effects of various solute transport mechanisms and identify which mechanism (i.e., advection and mechanical dispersion or molecular diffusion) is dominant for several reasons. One potential use of an estimate of the contaminant velocity is to 'reality check' the downgradient extent of the contaminant plume. For example, if the estimated contaminant velocity is 75 feet ft/yr and the release to ground water was believed to have occurred 20 years prior to a particular sampling event (based on available historical data, as typically provided in an RI report), detectable concentrations of fuel constituents that are not being attenuated would be expected to be present at least 1,500 feet from the release location. At many fuel-release sites, the actual plume length will be significantly less than the estimate, thereby providing an initial approximation of the effects of natural attenuation. As discussed in Section 5, estimates of contaminant velocities can also be used to provide the rationale for sampling frequency of monitoring wells. As an example, the travel time between a well located on a flow path that is 300 feet downgradient of another well would be on the order of 4 years assuming a contaminant velocity of 75 ft/yr. These types of travel time estimates are helpful for estimating when an observed change in contaminant concentration at one well can be expected to be observed in another well that is located on a downgradient flowpath.

Methods for quantifying the effects of advection through the calculation of ground-water velocity and retardation factors are discussed in Section 3.4.2, with supporting information provided in Section A.4.2 of Appendix A. Quantification of molecular diffusion effects is accomplished by looking up compound-specific values for the diffusion coefficient. Literature values for the diffusion coefficient of common fuel-related COCs are provided in Table A.1 of Appendix A. Once an estimate has been developed for contaminant velocity and the diffusion coefficient, calculation of the Peclet number for each site-specific COC should be performed to determine whether the dominant solute transport mechanism is advection (i.e., mixing is dispersion-dominated) or diffusion. As described in Section 3.4.2, use of the Peclet number approach suggests that, for BTEX compounds, the influence of diffusion-based transport should be considered as part of the evaluation of the dominant transport process in aquifers where the ground-water flow velocity is less than 30 ft/yr. Details regarding the calculation of the Peclet number are provided in Section A.4.2.2 of Appendix A.

At the vast majority of sites, advection will be identified as the dominant transport mechanism, implying that diffusion transport effects can be ignored and the assumptions inherent to most common solute degradation rate calculation methods and solute transport models (both of which assume an advection-dominated system) are valid. However, at a small percentage of sites, the ground-water flow velocity may be sufficiently low that diffusion is identified as a significant (or the dominant) contaminant transport mechanism. At the relatively small percentage of diffusion dominated fuel-release sites, decay-rate calculation methods (as

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described in Section 4.2.2.1.6) and, as needed, fate and transport models (as described in Section 4.3) that are valid for a diffusion-dominated system must be used.

4.2.2   Identify and Evaluate Chemical Data Trends

At fuel-release sites, chemical concentration data collected from soil, soil vapor, ground water, surface water, and (if present) LNAPL will vary with space and time due to various phenomena including contaminant transport, partitioning, degradation, and dilution. The process for evaluating MNA data is to first identify spatial and temporal chemical data trends and subsequently to interpret these data trends to demonstrate which phenomena are controlling or otherwise contributing to the observed contaminant plume behavior. Considering the relatively large number of chemical parameters that are recommended for collection as part of a fuel-release MNA evaluation, the decision on how to organize, analyze, and represent these data may not be readily apparent, particularly if there have been multiple points of release and/or the site hydrogeology is complex.

Although contaminant plume releases are 3-D in nature (i.e., have both lateral and vertical components), most approaches for interpretation, visualization, and evaluation of spatial variations group data into 2-D (or even 1-D) groups that are easier to comprehend and analyze. This section is intended to provide guidance on several common methods of data analysis and representation that have been found to be particularly useful at demonstrating the effects of MNA. Analysis and data representation methods are presented specifically for ground-water contaminant plumes, dissolved geochemical indicators, and changes in source area properties. Although not explicitly described in this protocol, the same analysis and data representation approaches described here can be adapted to evaluate soil and/or soil vapor data should this evaluation be required as a condition of achieving site closure.

4.2.2.1   Analysis of Dissolved Contaminant Concentrations

4.2.2.1.1   Contaminant Isoconcentration Contour Maps

The most common contaminant concentration data presentation technique is plotting contaminant concentrations on a site base map and drawing lines representing equal concentrations (isoconcentration or isopleths) to create 2-D contour maps. Contaminant contour maps should be prepared for benzene. Creation of benzene contour maps is recommended because this compound is the most common "risk-driver" for dissolved contaminant plumes at fuel-release sites. Creation of total BTEX contour maps provides complementary information to the benzene contour maps by depicting how the overall BTEX plume is behaving, relative to the behavior of the benzene plume. At most sites, total BTEX contour maps should be developed for each hydrostratigraphic unit that has been impacted by the fuel release. The decision on the number of total and/or individual BTEX compound contour plots over time should be based on consideration of the relative spatial completeness of a particular monitoring event data set, the overall duration of monitoring (and available data), and the site-specific data needs to support a defensible conclusion on plume stability. It is important that contaminant measurements from different hydrostratigraphic units be plotted separately, as dissolved contaminant concentrations resulting from a fuel release are found predominantly in the upper portion of the surficial aquifer, unless a significant vertical hydraulic gradient exists or the dominant transport mechanism is diffusion.

Plan-view contaminant contour maps facilitate interpretation of contaminant distribution using discrete data and, when used in conjunction with potentiometric surface maps, identification of the dominant direction of dissolved contaminant transport. At sites where

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comprehensive contaminant concentration data sets have been collected during multiple sampling events, visual evaluation of whether individual contaminant plumes (and/or the total BTEX plume) are stable, receding, or expanding is the first step in demonstrating MNA effectiveness. These maps also facilitate the identification of whether an approximate plume 'centerline' can be identified, and whether there are sufficient wells along this plume centerline to allow for application of 1-D analysis techniques (as described in Section 4.2.2.1.3). Another potential use of contaminant contour maps is to select the initial concentration condition for each contaminant (or total BTEX, if using a single solute model) when applying a numerical model to a site. The basic procedure for establishing this initial condition is to overlay the model grid on the contaminant concentration contour map and assign initial conditions based on the observed 'average' concentration within each particular cell, all of which can be done in an automated process incorporated into model platforms (e.g., BIOPLUME III, Groundwater Modeling System [GMS]) designed to aid the modeler in using site data to establish initial conditions prior to model execution.

In addition to plan-view contour maps, the use of cross-sectional (i.e., vertical 2-D) contour maps along the plume centerline is recommended at sites where significant variation in contaminant concentrations with depth is observed, particularly in the case where a nearby drinking water well is screened in a lower (presumably uncontaminated) aquifer unit. Use of cross-sectional maps, which should be overlain on the hydrogeologic cross-sectional maps described above, can be an effective way to illustrate preferential migration pathways and/or the degree to which low-permeability zones prevent contaminants from migrating to a deeper aquifer that may be exploited for water-supply purposes.

Based on the plume size, complexity, and available data, an experienced environmental professional should be used to develop the necessary contour maps either manually (with subsequent digitization into electronic format) or using one of the various commercially available software packages that can import columnar data containing the sample point name, coordinates (2-D or 3-D), and concentration and apply various kriging algorithms to interpolate contaminant concentrations contours. Whichever contouring method is used, it is important to have the plume bounded in all directions (i.e., below detection measurements on the upgradient, downgradient, and cross-gradient sides).

4.2.2.1.2   Pie Diagrams on Map

An alternate method of illustrating changes in contaminant plume composition with space is to plot pie diagrams on a plan view site map (2-D representation) or along the contaminant plume centerline (1-D representation) to show how plume composition changes with space. For a typical fuel-release site, the base map for this pie-diagram approach could be the total BTEX contour map overlain on the site base map. Pie diagrams of individual BTEX contaminants could then be developed where the overall size of the 'pie' is correlated to total BTEX concentration, while the size of individual 'slices' that make up the pie represents the percentage of the total BTEX that any individual constituent contributes.

4.2.2.1.3   One-dimensional Concentration Graphing

At sites where contaminant transport is dominated by advection, plan view contaminant contour maps and potentiometric surface maps can be used to identify whether a contaminant flow path corresponding to the contaminant plume centerline can be identified. If a dominant flow path has been identified, these maps can further be used to identify which wells are located along the plume centerline, and plots of contaminant concentration-versus distance-from the source area can be developed. At sites where a 1-D flow path can be identified, numerous

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analytical techniques can be applied to 1-D concentration data plots to develop estimates of degradation rates as described in Section 4.2.2.1.6.

At sites where contaminant transport is dominated by diffusion, 1-D plots of contaminant concentrations versus the radial distance from the source area can be used to confirm that contaminants are generally dispersing uniformly in all directions. Uniform radial migration of contaminant is expected in aquifers where diffusion dominates transport because concentration gradient, not hydraulic gradient, drives contaminant transport. For diffusion-dominated aquifers, the biodegradation rate for BTEX compounds will typically be greater than the diffusion-driven rate of contaminant transport. In this case, biodegradation rates for individual COCs may be estimated using the concentration versus time rate constant (k_{point}) described in Section 4.2.2.1.6.

4.2.2.1.4 Time Series Graphing

Perhaps the simplest (and often most compelling) evaluation of fuel-release plume dynamics is to plot contaminant concentrations at a well (or series of wells) versus time. This analysis can be performed on individual or lumped contaminant concentrations, and provides a straightforward method for visually observing if contaminant concentrations at most or all monitoring points are declining over time. The simple observation that contaminant concentrations are decreasing at all monitoring points (and especially that concentrations are not increasing at downgradient points) provides strong evidence that a dissolved contaminant plume is attenuating.

Depending on site goals and data needs, simple regression models (commonly first-order) can be applied to each data set to estimate the overall contaminant decay rate at a given point and provide an estimate of the goodness-of-fit (e.g., R-squared coefficient). Use of this and other approaches for estimating various degradation rates is described in Section 4.2.2.1.6

4.2.2.1.5 Statistical Trend Analysis

Prior to performing rigorous statistical analyses of environmental data, an assessment should be made of whether a combination of the relatively simple data representations and analyses described above is sufficient to convince site regulators and other stakeholders that natural attenuation process are protective of potential receptors, reducing contaminant mass, and maintaining a stable or receding plume. In the event that these criteria, described as the first line-of-evidence in the OSWER directive on MNA (USEPA, 1999a), are demonstrated, additional statistical analysis may not be required. At sites where data trends are not sufficiently clear, however, more advanced statistical analysis techniques may be required.

Three techniques for statistical analysis of environmental data (Mann-Kendall [MK] Test, Sen's Test, and Method of Moments) are described here in terms of data output capabilities, data interpretation, and level of effort required to perform each type of analysis. In general, application of the MK and Sen's Tests to environmental data is relatively simple through the use of either existing software (e.g., MAROS) or by the development of custom 'templates' that employ statistical routines offered in several commercially available spreadsheets. In addition, interpretation of MK and Sen's Test results can be readily performed by most environmental professionals. If appropriate, application of the method of moments analysis technique for environmental field data will be greatly facilitated using an existing software interface, such as the one incorporated into the latest version of MAROS (AFCEE, 2002; Aziz *et al.*, 2002). Interpretation of results from a method of moments analysis is more complicated than the other statistical tests described here, and it is therefore recommended that the results of this test be interpreted by an environmental professional or statistician with experience using the method of

moments approach. Techniques for statistical analysis of environmental data have been well-described previously, and users of this protocol are referred to USEPA (1993), Gibbons (1994), and Gilbert (1987) for additional information.

Mann-Kendall Test

The MK nonparametric estimator for trends (Mann, 1945; Kendall, 1975; Gilbert, 1987) can be used to assess whether contaminant concentrations at a given monitoring point are increasing or decreasing with time. This test is well-suited for environmental data because it requires only small sample sizes and does not assume any underlying distribution for the data. The output of the test is the S statistic. The null hypothesis of this test is that no trend exists in the data. Hypothesis testing to assess the presence of a trend can only be performed for data sets consisting of four or more data points, with positive and negative S statistics serving as indicators of increasing and decreasing concentration trends, respectively. By using the S-statistic to assign statistical confidence to the conclusions of these tests, a quantitative method of determining if the concentrations are increasing or decreasing with time is obtained that can be used to provide statistical support to a qualitative visual inspection of the time-series plot.

Sen's Nonparametric Estimator of Slope

If a linear trend is present, the true slope (change per unit of time) of the time-series graph for a sampling station may be estimated using a simple, nonparametric procedure developed by Sen (1968) and described by Gilbert (1987). Unlike the true slope estimated by computing the least-squares estimate of the slope by linear regression methods, Sen's method is not greatly affected by data errors or outliers, and the slope can be computed when data are missing. Sen's estimator is closely related to the MK test, and the resulting slope can be used to assess temporal trends in pre- and post-remediation ground-water quality data. Similar to the S statistic discussed for the MK test, positive and negative slopes indicate increasing and decreasing trends, respectively. The magnitude of the slope is an indicator of the rate at which dissolved contaminant concentrations are changing (e.g., a slope of -1,000 indicates more rapid decreases than a slope of -500).

Method of Moments Analysis

The method of moments approach, as described in USEPA (1998d), Aziz *et al.* (2002), and GSI (2003), is a relatively novel approach to evaluating overall contaminant plume dynamics. In summary, the analysis of moments can be used to help quantify overall plume trends by calculating values for characteristic parameters such as:

- Change in dissolved mass over time (Zero-order Moment);
- Change in the location of the center of mass over time (First-order moment); and
- Change in plume distribution over time (Second-order moment).

For plumes that are naturally attenuating, the results of zero-order moment calculations should theoretically indicate that the overall estimated contaminant mass is continually decreasing over time. In practice, and as described by GSI (2003) following application of the method of moments approach to a dissolved contaminant plume at McClellan Air Force Base (AFB), the zero-order moment estimation for contaminant mass is subject to significant fluctuations due to sensitivity to: 1) temporal changes in concentrations at the most contaminated wells and 2) variability in the location of sampled monitoring wells or the sampling method during different events. Similarly, the expected trend for the location of the center of mass of a naturally attenuating plume calculated using the method of moments analysis technique should be that the

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center of mass is moving downgradient for an expanding plume, upgradient for a contracting plume, and is relatively steady for a stable plume. In practice, this calculation is subject to the same sensitivities as the plume mass estimate. In addition, it is interesting to note that implementation of a source removal action that reduced contaminant source area concentrations (or even natural source weathering) may result in an abrupt downgradient shift of the center of mass which could lead to the erroneous conclusion that the contaminant plume has started to expand, even though data collected over a longer term should eventually show that the plume center of mass is receding.

Due to the relatively new application of the method of moments approach to estimating dissolved ground-water plume characteristics, and the challenges that interpreting results presents, it is too early to know whether this approach will prove to be cost-effective for demonstrating plume stability and achieving site exit strategy goals at fuel-release sites. Given the state of practice, it is recommended that available site data be carefully evaluated to determine whether multiple time-series data sets of sufficient spatial coverage are available prior to applying this approach to fuel-release sites, and that the results of this approach be carefully evaluated by an experienced environmental professional prior to drawing conclusions on method of moments analysis findings.

4.2.2.1.6   Methods for Estimating Site-specific Degradation Rates

In many cases, degradation of fuel hydrocarbons can be approximated using first-order kinetics. Estimation of degradation rate constants is important to both demonstrating that natural attenuation processes are occurring and in making future predictions on expected MNA performance. It is important to recognize that 1) there are multiple types of degradation rate constants, 2) there are several rate constant estimation methods, and 3) each type of degradation rate constant has a different use when estimating future contaminant plume performance. The text provided here is intended primarily to provide an understanding of how the various degradation rate constants can be used, rather than provide specific details on how to calculate each constant. For more information on calculation of the various degradation rate constants, the reader is directed to Appendix C-3 of the original protocol (AFCEE, 1995) and several recent publications that summarize estimation of degradation rates, including USEPA (2002d), Wiedemeier *et al*. (1999), and Chapelle *et al*. (1996b). In addition, several software packages, including BioTrends (available from www.waterloohydrogeologic.com), NAS (Chapelle *et al*., 2003), and RaCES (Budge *et al*., 2003), have been developed to assist environmental professionals in calculating degradation rate constants.

As described in USEPA (2002d), the three common types of degradation rate constants that are used in MNA evaluation studies can be defined as:

- Concentration versus time rate constants (k_{point}), which can be used to estimate how quickly site remediation goals are expected to be met at specific monitoring points;

- Concentration-versus-distance 'bulk' attenuation rate constants (k), which can be used to evaluate plume dynamics and estimate required reductions in source concentrations to attain a remediation goal at a given downgradient compliance point; and

- Biodegradation rate constants (λ), which can be used in solute fate and transport models to explicitly simulate biodegradation effects on contaminant migration.

Although k_{point} does not correspond to any specific natural attenuation mechanism, estimation of this parameter does provide a quantitative assessment of the combined effects of contaminant transport, sorption, dilution, and degradation processes that have been occurring over time at a

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given point within the contaminant plume. k_{point} can be estimated as the slope of the best-fit line through a semi-log plot of concentration versus time data (Section 4.2.2.1.4) for each monitoring point where historical data exists, and has the units of time^{-1}. Perhaps the most important use of k_{point} is to estimate the remediation timeframe required to meet an applicable regulatory standard at any given location where contaminant concentrations currently exceed this standard. Based on experience at numerous fuel-release sites, degradation rates of BTEX contaminants are generally faster in the dissolved portion of the plume relative to the source area, and the most persistent contaminant concentrations are typically observed in monitoring wells located in the source area. Based on this experience, one method for estimating the remediation timeframe (i.e., the time required for contaminant concentrations at all locations to reach a specified target concentration) is to apply the k_{point} approach to source area monitoring wells and use the longest time estimate as the overall site remediation timeframe estimate for each COC. Although this approach to estimating remediation timeframes is generally applicable to BTEX and most other common fuel constituents, this approach may not be conservative for MtBE. The reason this 'source area depletion' approach for estimating remediation timeframes for highly soluble and/or relatively recalcitrant compounds, such as MtBE, may not be conservative is that the slow biodegradation rate of relatively recalcitrant compounds in the dissolved contaminant plume may imply that concentrations within the downgradient plume may still be above a specific regulatory target concentration, even though the contaminant has been relatively rapidly depleted out of the source area due to its high solubility. It is also noted that k_{point} cannot be used to estimate contaminant distribution across the site or be used to predict the effects of a change in concentration at another location because estimation of this parameter is based on data from a single point in space.

k is analogous to k_{point} in that this parameter is also a quantification of the combined effects of contaminant transport, sorption, dilution, and degradation, but is different from k_{point} in that the quantification of k is function of space rather than time. k is calculated by multiplying the slope of the best-fit line through a semi-log plot of concentration-versus-distance along a plume centerline (Section 4.2.2.1.3) by the contaminant velocity to obtain units of time^{-1}. Note that the slope of the best-fit line has been referred to as the natural attenuation capacity (NAC) by Chapelle and Bradley (1998), and has the units of length^{-1}. The primary limitations of calculating k (or NAC) using this approach are that 1) monitoring wells used in this calculation need to be along the same ground-water flowpath (preferably along the plume centerline) and 2) individual estimates do not account for any changes in degradation rate that may be occurring over time. Although calculation of k may be helpful when attempting to evaluate spatial changes in the bulk degradation rate, Chapelle and Bradley (1998) provide an example of how to use the NAC estimate (rather than k) to estimate how much source reduction is required to achieve a specified target concentration at a given downgradient point of compliance. As such, the NAC approach could be used to provide a concentration target for active source remediation (MNA with source treatment approach) if current performance objectives are not being met at a given downgradient location.

Estimates for λ can be used to provide a quantified estimate of destructive natural attenuation mechanisms, and are necessary to simulate the fate and transport of BTEX and other fuel-related compounds dissolved in ground-water using mechanistic fate and transport models. Although biodegradation of BTEX compounds has been shown in the laboratory to follow Monod kinetics, approximation of fuel constituent biodegradation rates using a first-order kinetics model is the most common approach used in practice. To calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution and volatilization. Two methods for determining first-order rate constants have been described in Appendix C-3 of

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the original protocol, and are still commonly used. One method involves the use of a biologically recalcitrant compound found in the dissolved BTEX plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (1995), assumes a steady-state contaminant plume with a continuous source that uses a 1-D steady-state analytical solution to the advection-dispersion equation presented by Bear (1979) to calculate λ. As acknowledged by Buscheck and Alcantar (1995) and elaborated upon by McNab and Dooher (1998), the assumptions inherent to using the Buscheck and Alcantar inverse estimation approach do not account for the effects of lateral dispersion (i.e., 2-D transport), the presence of normal site heterogeneities (e.g., changes in direction or magnitude of ground-water velocity), and the effects of a decaying source, all of which could lead to an overestimation of λ when using this method. In addition, the method of Buscheck and Alcantar assumes that advection is the dominant transport mechanism, and is therefore not theoretically valid for sites where contaminant transport is dominated by diffusion. A third method for estimating λ is to calibrate a ground-water solute transport model that explicitly accounts for advection, dispersion, diffusion, sorption, and biodegradation (e.g., BIOSCREEN, BIOPLUME III, MT3DMS, RT3D, SEAM3D) by adjusting λ. Considering the variability of biodegradation rates that may be estimated by any of these approaches, it is recommended that the sensitivity of model-estimated biodegradation rates to other site parameters (e.g., ground-water velocity, retardation factors, simulated source condition) be systematically investigated and reported. At sites where establishing the rate of contaminant degradation is critical to the acceptance of MNA (e.g., sites where there is relatively limited historic data and/or where modeling will be the primary basis for MNA evaluation), it is advisable to estimate and report contaminant biodegradation rates using a variety of methods to develop a range of site-specific biodegradation rates.

4.2.2.2   Analysis of Geochemical Indicator Data

At sites where fuel contaminants reach ground water, biodegradation of fuel constituents will produce measurable changes in ground-water chemistry that can be used to identify the type and extent of biodegradation processes that are occurring. The following text discusses how to present and interpret site-specific geochemical indicator data (i.e., the second line of evidence) to support and complement the interpretation of plume stability and biodegradation potential developed using contaminant concentration data (i.e., the first line of evidence).

The first step in processing geochemical indicator data should be to organize these data in tabular format so that a well-by-well assessment of the local redox condition can be performed. During the tabulation process, it is recommended that measured parameters be grouped by role in the interpretation of redox condition, and that wells be grouped as background wells, source area wells, dissolved plume wells, and downgradient wells. An example of parameter groupings could be:

- Electron acceptors: DO, nitrate, sulfate, carbon dioxide (if measured);

- Reaction endproducts: iron(II), manganese(II) (if measured), hydrogen sulfide (if measured), methane; and

- Other geochemical indicators: ORP, temperature, pH, alkalinity, conductance, turbidity.

By reading 'down' a column of data for each well, an evaluation of the redox condition can readily be performed. For example, the first level of analysis would be evaluating whether conditions are aerobic or anaerobic (e.g., presence or absence of DO), with a second level of evaluation for anaerobic redox condition (e.g., conditions are moderately reducing [nitrate- or

iron-reducing] or strongly reducing [sulfate-reducing or methanogenic]). As part of the redox condition assessment, ORP values should be compared with the conclusion drawn from looking at electron acceptor and reaction endproduct data. Figure 3.3 provides an indication of the 'typical' range of ORP values anticipated for each redox condition. During the review of 'other geochemical indicators', data collected on temperature, pH, and alkalinity should be reviewed to confirm that conditions are conducive to biodegradation (e.g., pH is relatively neutral). Concurrent with evaluation of redox conditions at individual wells, observations at background (i.e. upgradient and/or cross-gradient) wells should be compared with wells in and downgradient of the plume to observe how redox conditions within the plume compare with 'background' conditions. For a typical fuel-release site (e.g., release into an unconfined aquifer that is naturally oxidizing), the most strongly reduced conditions should be located in the source area, with a gradual transition through less reducing conditions and eventually oxidizing conditions as one moves outside the plume footprint.

For small contaminant plumes that are stable (or receding) and have relatively limited geochemical indicator data, presentation of geochemical indicator results in tabular format with a corresponding discussion on the overall assessment of redox conditions inside and outside the contaminant plume may be sufficient to support observations of natural attenuation made during the contaminant concentration data analysis discussed above. For larger and/or more complex sites, developing visual representations of geochemical indicator data is recommended to facilitate interpretation of the spatial occurrence of various biodegradation processes and their effects on contaminant fate and transport. Visual representations of geochemical indicator data could be as simple as annotating existing 2-D contaminant contour maps with geochemical indicator data values or as complex as generating individual 2-D contour maps for each geochemical indicator parameter. At sites where a dominant contaminant flowpath exists, geochemical indicator concentrations at wells along the plume centerline can be used to develop 1-D concentration-versus-distance plots, as described for contaminants in Section 4.2.2.1.3. If multiple time sets of geochemical indicator data are available, a well-by-well comparison should also be made to determine whether redox conditions are stable or changing over time. The decision on how much time and effort should be spent creating visual representations of geochemical indicator parameters will be site-specific and based, at least in part, on how convincingly the contaminant concentration analysis can demonstrate plume stability (or recession) and whether geochemical indicator data will be used in the calibration of a solute fate and transport model. If visual representation of geochemical indicator data is deemed appropriate, contour maps and/or concentration-versus-distance data plots should be prepared for electron acceptors consumed (DO, nitrate, and sulfate) and reaction endproducts produced (iron[II] and methane) during biodegradation. In addition, a visual representation of alkalinity data may be prepared if these data have been measured.

Regardless of which data representation technique is used, electron acceptor, reaction endproduct, and alkalinity data provide the most direct evidence of the occurrence of MNA at a fuel-release site. During aerobic biodegradation, DO concentrations will decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will decrease to levels below background, and the concentrations of degradation reaction byproducts (e.g., iron[II] and methane) should increase to levels above background. The development of electron acceptor contour maps or 1-D concentration-versus-distance plots allow interpretation of the distribution of terminal electron acceptor processes. Thus, electron acceptor contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors. In addition, electron acceptor contour maps can be used to identify the initial conditions for input

into a mechanistic solute fate and transport model that can be used to support future predictions of MNA performance. Note that BIOSCREEN, BIOPLUME III and the various numerical models based on the Modular Three-dimensional Transport (MT3D) code (e.g., MT3DMS, RT3D, SEAM3D) will require direct input of each of these parameters if sequential electron acceptor conditions are explicitly modeled.

Similarly, the development of reaction endproduct contour maps or 1-D concentration-versus-distance plots provides visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various metabolic byproducts. Finally, a contour map or 1-D concentration-versus-distance plot should be prepared for total alkalinity (as $CaCO_3$). Respiration of DO, nitrate, iron (III), and sulfate tends to increase the total alkalinity of ground water. Thus, the total alkalinity inside the contaminant plume generally increases to levels above background. This map will allow visual interpretation of alkalinity data by showing the relationship between the contaminant plume and alkalinity. If alkalinity concentrations within the contaminant plume are generally less than background concentrations, historic data on pH should be reviewed to see if pH is decreasing over time due to consumption of the acid buffering capacity of the natural formation. If both alkalinity and pH are observed to be decreasing with time, biodegradation processes may be less effective at maintaining plume stability, and contaminant concentrations should be carefully reviewed to see if there is a corresponding change in plume dynamics.

Another method for incorporating geochemical indicator parameter analysis into evaluation of MNA is to perform calculations of the assimilative capacity of ground water and, if following procedures recommended by the AMIBA protocol (AFCEE, 2000b), of soil. The assimilative capacity (also referred to as biodegradation capacity by Wiedemeier *et al.* [1999] or oxidation capacity by Barcelona and Holm [1991] and Heron *et al.* [1994]) is defined as the mass of contaminant that would be degraded if all of the available electron acceptor mass was consumed. Wiedemeier *et al.* (1999) make a further distinction by defining the expressed assimilative capacity as the portion of the total assimilative capacity that has been consumed within the contaminant plume, calculated by summing up the individual assimilative capacities for each electron accepting process. Appendix C of the original protocol (AFCEE, 1995) and Wiedemeier *et al.* (1999) describe in detail how to use the stoichiometric relationships presented in Appendix A, and the difference between electron acceptor/reaction endproduct concentrations measured within the contaminant plume with those measured in a background location to estimate total and expressed assimilative capacity. Note that this approach to calculating expressed assimilative capacity is comparable to the instantaneous reaction model for simulating contaminant degradation in the BIOSCREEN and BIOPLUME III solute transport models.

It should be noted that sole use of aqueous-phase concentrations in calculating assimilative capacity most likely underestimates the true assimilative capacity of iron(III)-reducing and methanogenic processes. This underestimation is expected because the effects of these two processes are quantified using the concentrations of aqueous reaction endproducts, rather than measurements of the electron acceptors themselves. For iron(III)-reduction, calculation of assimilative capacity using the aqueous reaction byproduct (ferrous iron) concentrations will underpredict the true assimilative capacity of this process because ferrous iron is likely to react with anions commonly found in ground water and precipitate out of the aqueous phase, which results in a assimilative capacity calculation that is based on a concentration that is significantly less than what would have been measured if ferrous iron had remained in the aqueous phase. To address this limitation for iron(III)-reduction, AFCEE (2000b) developed the AMIBA protocol that provides guidance for sampling, analysis, and data interpretation methods that can be used to

incorporate the effects of solid-phase electron acceptors (e.g., iron(III)) by using direct measurements of solid-phase bioavailable iron. Quantification of the assimilative capacity of methanogenesis is more problematic because methane is highly volatile (i.e., measured concentrations are expected to be lower than total production), and an unlimited supply of the electron acceptor for methanogenesis, carbon dioxide, is generally considered to be present within the contaminant plume.

However the expressed assimilative capacity is calculated, this value can be compared with the maximum dissolved source area concentration and/or the estimated mass of contaminant remaining in the subsurface to evaluate how natural attenuation would be expected to be sustained on a long-term basis. If the more simplistic and inexpensive aqueous-phase approach is used (i.e., without quantification of solid-phase bioavailable iron), it is recommended that this comparison primarily be qualitative in nature. For example, if the expressed assimilative capacity is significantly less than the maximum observed dissolved source area contaminant concentration, significant contaminant migration out of the source area may be expected, and source concentration reduction measures should be considered. A calculation of an expressed assimilative capacity that is significantly larger than maximum observed source concentrations would suggest that an MNA alternative is likely to be protective of downgradient receptors (i.e., that there is sufficient assimilative capacity in the aquifer to degrade all of the dissolved COCs). In this second case, the decision on whether source reduction offers a cost-effective way of meeting the overall goals of the site exit strategy should be based primarily on the rate of degradation, rate of contaminant transport, and proximity to downgradient receptors, and less on concerns of aquifer assimilative capacity. In cases where a more rigorous, quantified assessment of assimilative capacity is required to support the goals of the site exit strategy through quantitative demonstration of long-term sustainability, performing additional site characterization activities to better define 1) the mass of contaminant remaining in the subsurface, 2) the mass of bioavailable iron (following the AMIBA protocol), and 3) the mass flux of aqueous electron acceptors into the contaminant plume (from recharge and influx of upgradient ground water) is recommended.

4.2.2.3   Evaluation of Changes in Source Properties

If mobile LNAPL is present, a site map showing the horizontal extent and apparent LNAPL thickness should be prepared. Contour maps of LNAPL thickness allow interpretation of the distribution and the relative transport rate of LNAPLs in the subsurface. In addition, these maps will aid in partitioning calculations and solute fate and transport model development. It is important to note that, because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, LNAPL thickness observations made at monitoring points may not provide an accurate estimate of the actual volume of mobile and residual LNAPL in the aquifer. To accurately determine the distribution of LNAPLs, it is necessary to take continuous soil cores or to use CPT testing coupled with laser-induced fluorescence. For additional information on the relationship between actual and apparent LNAPL thickness, users of this protocol are referred to Appendix C of the original protocol (AFCEE, 1995).

In addition to mapping changes in mobile LNAPL lateral extent and thickness, calculation of the source decay rate is a necessary step to estimating the remediation timeframe for dissolved fuel-related contaminants (primarily BTEX, MtBE, and naphthalene). At sites where only residual LNAPL is present, application of the time-series data plotting procedure and k_{point} analysis procedures should be sufficient to develop the estimate for when contaminant concentrations in the source area would be expected to reach a specified target concentration. At

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sites where mobile LNAPL is also present, periodic measurements of mobile LNAPL composition can be combined with source area dissolved concentrations and applied to a model such as SourceDK™ (GSI, 2004) to evaluate the effects of source weathering and to estimate the time of remediation, based on the estimated time for dissolved contaminants in the source area to reach a specified aqueous-phase concentration.

4.3   MODELS OF PLUME BEHAVIOR THROUGH TIME

Solute fate and transport models can be useful tools for evaluating natural attenuation at fuel-release sites. These models can be used as a predictive tool to evaluate future dynamics of the dissolved contaminant plume, predict contaminant concentrations at a specified downgradient location (e.g., monitoring well), and assist in developing an estimate for the expected time frame to meet specific remediation goals. Models can also be used as an interpretive tool to help understand and quantify the effects of various natural attenuation processes. Mechanistic models (i.e., models that simulate specific contaminant fate and transport processes, such as advection, dispersion, diffusion, sorption/desorption, biodegradation, NAPL dissolution) are particularly useful as interpretive tools because the process of calibrating mechanistic models to historical data sets often provides useful insight into which processes have the biggest impact on contaminant plume dynamics.

Prior to initiating a modeling effort in support of an MNA evaluation, it is recommended that both the purpose and primary questions that need to be answered by modeling be identified. Once the model purpose and desired outcomes have been identified, an assessment of existing data should be made to determine which types of models are appropriate given the physical characteristics of the site and whether sufficient data exists to develop a scientifically-defensible representation of site conditions. The following text is intended to provide guidance on determining whether a model is really necessary to achieve a desired exit strategy and, if so, what types of models may be appropriate. For additional information on modeling natural attenuation, the user may wish to refer to Appendix D of the original protocol (AFCEE, 1995) or recent summaries of how to apply models for natural attenuation, as described in Wiedemeier *et al*. (1999) and Bedient *et al*. (1999).

4.3.1   Is a Model Really Necessary?

One of the first questions to ask before proceeding with implementation of a solute transport model is: "Is a model really necessary?" The answer to this question will depend on several factors, including the rate of plume expansion (if any), the locations of potential receptors, and the amount of available historical contaminant concentration data that can be used to demonstrate that the contaminant plume is stable or receding over time. For example, if there are abundant historical data available for the site, and these data show that the dissolved BTEX plume has reached a steady-state configuration or is receding, then a solute transport model is not necessary to determine if potential receptors will be impacted. However, a model of this site would allow an investigator to estimate how long it will take for the plume to entirely degrade. If on the other hand, the plume is close to a potential receptor and there is little historical data available, then a solute transport model, used in conjunction with the appropriate data, can be useful in predicting solute fate and transport, and in developing estimates for remediation timeframes and the potential for further downgradient migration.

Two questions will invariably arise during an MNA evaluation. These questions are: 1) will potential receptors be impacted by the contaminant plume and 2) how long will the contaminant plume persist? If the proponent of MNA is unable to provide plausible and defensible answers to these questions (either with or without a solute transport model), it is unlikely that MNA will be

accepted by regulators. When properly used with an adequate database, solute transport models can help provide answers to these questions and aid in reaching the site exit strategy.

4.3.2 Pre-modeling Evaluation

As described in Spitz and Moreno (1996), modeling efforts for the simulation of solute fate and transport generally share the following common components:

- The natural system for which the model is designed;

- A CSM that is an idealized representation of the natural system;

- A mathematical model that represents various mechanisms that control system performance;

- A solution technique (analytical or numerical) for the mathematical model;

- Calibration of the model solution to observed measurements of the natural system;

- Validation of model prediction accuracy through use of additional observed measurements; and

- Simulation of future conditions, based on parameters used to developed a calibrated mathematical solution of the CSM.

Model application in support of MNA evaluations at a fuel-release site will consist of most, if not all, of these components. For the purposes of discussion, a natural attenuation model is defined as a mathematical model that, at a minimum, simulates dissolved solute advection, dispersion, sorption, and biodegradation. In addition, assumptions on whether contaminants will be simulated as 'lumped' compounds (e.g., total BTEX) or individual compounds, and whether specific electron acceptor processes will be simulated using measured electron acceptor concentrations to 'limit' the amount of biodegradation by each process, need to be made as part of the model evaluation process. Based on these decisions, assumptions will be needed to establish the initial and boundary conditions for each solute that will be included in the model. These initial and boundary conditions will need to include assumptions about starting concentrations in the source area and how the contaminant source will be simulated. The following text provides an overview of the types of information required as input parameters to simulate each of these processes.

4.3.2.1 Ground-water Flow

Based on the evaluation of site-specific transport effects described in Section 4.2.1, a decision on whether contaminant transport is dominated by advection or diffusion will aid in eliminating models that neglect effects of diffusion as part of the model assumptions. For the majority of sites, advective transport (i.e., the existence of defined flow paths of contaminant transport) will be the dominant transport mechanism. At these sites, the next decision will be whether ground-water velocities across the entire contaminant plume can be assumed to be 1-D and uniform (thereby allowing for use of an analytical solution) or if seasonal variations in hydraulic flow direction and/or heterogeneities in the porous media will require use of a 2-D or 3-D ground-water flow model (which generally will require use of a numerical model). If a 1-D uniform flow model is acceptable, calculation of the ground-water flow velocity can be performed as described in Section 3.4.2. If either a 2-D or 3-D flow model is required, numerical models will require input for porosity, hydraulic conductivity, and hydraulic gradient which can be either uniform or non-uniform (with respect to space) and either steady or unsteady (with respect to time). For numerical models where uniform, steady flow can not be assumed, results of the

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ground-water flow model will need to be calibrated to existing ground-water elevation data prior to simulation of solute fate and transport.

4.3.2.2   Sorption

Nearly all models used to simulate natural attenuation of fuel hydrocarbons assume that sorption is a linear, isothermic process that can be quantified by calculating a retardation coefficient, which is defined as the ratio of ground-water velocity to contaminant velocity. Methods for calculating the retardation coefficient are described in Section 3.4.2.3 and Section A.4.2.3 of Appendix A.   When accounting for sorption in analytical models, either the contaminant velocity or retardation coefficient and ground-water flow velocity will be required input for simulating sorption.   For numerical models, some or all of the parameters used to calculate the retardation coefficient (e.g., porosity, distribution coefficients, bulk density) will be required input, and can be specified either uniformly (homogeneous assumption) or non-uniformly (if sufficient heterogeneity is quantified within a single hydrostratigraphic unit, or multiple hydrogeologic strata are being simulated).

4.3.2.3   Biodegradation

Biodegradation rates for each simulated contaminant solute also will be required.   As described in Section 4.2.2.1.6, biodegradation rates are commonly estimated using first-order approximations that can be used as direct input into many natural attenuation models. As with contaminant transport and sorption parameters, biodegradation rates may be input as either uniform or non-uniform values. The choice of whether to use a uniform or non-uniform value for biodegradation rate constants will be dictated by 1) the ability of the model being used to accept non-uniform data input and 2) the simplifying assumptions used to choose an appropriate natural attenuation model.

Some models also offer alternate methods of simulating biodegradation that are more complex than the first-order approach.   Specifically, these alternate models account for the impact of contaminant and, in some models, electron acceptor concentrations on model degradation kinetics. For models that simulate biodegradation using Monod kinetics, input parameters will include the maximum contaminant utilization rate and half-saturation constants for contaminants and, in some models, electron acceptors.   The maximum contaminant utilization rate is that rate at which a contaminant would degrade if there is no limit on the available substrate (i.e., contaminant) or electron acceptor.   The maximum contaminant utilization rate will be equal to a first-order rate in cases where contaminants and electron acceptor concentrations do not limit the rate of biodegradation.   Half-saturation constants are used to simulate the effects of substrate or electron acceptor limitations on biodegradation rates. Mathematically, half-saturation constants are defined as the chemical concentration that will cause the observed biodegradation rate to be exactly one-half of the maximum contaminant utilization rate.   To estimate maximum contaminant utilization rates and half-saturation constants, contaminant concentration and electron acceptor data require further analysis by an environmental professional that has experience calibrating Monod-kinetics biodegradation models or use of literature values. For models that use instantaneous reaction kinetics or dual-Monod kinetics, the stoichiometric coefficients provided in Appendix A will be either embedded into the model (if the model is compound-specific) or input by the user.

4.3.2.4   Contaminant Source

The various methods that are used to simulate the contaminant source for natural attenuation models include constant concentration sources, decaying concentration sources, and explicit

simulation of LNAPL mass weathering through use of an equilibrium-based model using a first order dissolution coefficient. As described in Sections 3.3.2.2 and 4.2.3.3, dissolution of contaminants from the LNAPL to the dissolved phase is expected to decrease over time due to the effects of source weathering, implying that models that use either the decaying concentration source or explicit simulation of LNAPL dissolution are most representative of field observations. If additional information on how to incorporate decaying source terms into analytical models for simulation of natural attenuation is desired, the reader is directed to Appendix D-3 of the original protocol (AFCEE, 1995).

4.3.3   Overview of Contaminant Fate and Transport Models

Simulating MNA allows prediction and/or interpretation of the migration and attenuation of the contaminant plume through time. MNA modeling is a tool that allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that MNA is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterization will improve the validity of the modeling results.

4.3.3.1   Selecting an Appropriate Model

Partial differential equations that describe solute transport can be solved analytically or numerically. Analytical models provide exact, closed-form solutions, and numerical models provide approximate solutions. The type of model selected to simulate site conditions will depend on the results of data review and conceptual model development. Solute transport modeling is both an art and a science. The "art" involves the ability to select the most reasonable set of assumptions that will yield a model that is not too complex to be solved by available mathematical techniques, yet is sufficiently detailed to accurately represent the system being modeled. A balance between simplifying assumptions and actual subsurface conditions must be reached to allow successful simulation of contaminant fate and transport.

In some cases, straightforward analytical models of contaminant attenuation are adequate to simulate MNA. In other cases, numerical models will be required due to the need to simulate complex ground-water flow and contaminant transport systems that exhibit irregular geometry and significant aquifer heterogeneity. Note that many of the assumptions required for the analytical solutions are not necessary when numerical techniques are used to solve the governing solute transport equation.

Figure 4.1 shows a decision process that can be used to determine if an analytical or a numerical model is most appropriate to simulate site conditions. The specific modeling objectives of the project, the available data, and the CSM should be the primary factors governing model selection. Much of the success of solute fate and transport modeling lies in the ability to properly conceptualize the processes governing contaminant transport, to select a model that simulates the most important processes at a site, and to achieve model predictions that reasonably correlate to observed conditions. Any model used for an MNA demonstration should be properly validated through sufficient application at a variety of field sites.

Since publication of original protocol (AFCEE, 1995), analytical models, such as BIOSCREEN (USEPA, 1996a; GSI, 1997), BioTrends (www.waterloohydrogeologic.com), and NAS (Chapelle *et al*., 2003), have either been developed or updated and revised to aid in interpreting natural attenuation data by incorporating methods for estimating source decay rates, natural attenuation rates of dissolved contaminants, and/or clean up timeframes. Concurrently,

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FIGURE 4.1
DECISION PROCESS FOR MODEL SELECTION

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┌──────────────────┐                          ┌──────────────────────┐
│  Reassess Goals  │─────────────────────────▶│ Are Order of Magnitude│
│  and Data Needs  │                          │ Predictions Acceptable?│
└──────────────────┘                          └──────────────────────┘
                                                  No │          │ Yes
                                                     │          ▼
                                        ┌───────────────────────────────────────┐
                                        │ Is it Reasonable to Assume That Media   │
                                        │ Properties Are Uniform, and Do Not      │
                                        │ Vary Spatially?                         │
                                        └───────────────────────────────────────┘
                                                  No │          │ Yes
                                        ◀────────────┘          ▼
                                        ┌───────────────────────────────────────┐
                                        │ Is it Reasonable to Assume That the Flow│
                                        │ Field is Uniform, Steady, and Regular?  │
                                        └───────────────────────────────────────┘
                                                  No │          │ Yes
                                        ◀────────────┘          ▼
                                        ┌───────────────────────────────────────┐
                                        │ Is it Reasonable to Assume That the     │
                                        │ Site Geometry is Regular?               │
                                        └───────────────────────────────────────┘
                                                  No │          │ Yes
                                        ◀────────────┘          ▼
                                        ┌───────────────────────────────────────┐
                                        │ Is the Conceptual Model Relatively      │
                                        │ Simple in Configuration?                │
                                        └───────────────────────────────────────┘
                                                  No │          │ Yes
                                        ◀────────────┘          ▼
                                        ┌───────────────────────────────────────┐
                                        │ Does the Pollutant Have Approximately   │
                                        │ the Same Density as Water?              │
                                        └───────────────────────────────────────┘
                                                  No │          │ Yes
                                        ◀────────────┘          ▼
                                                      ┌──────────────────────┐
                                                      │  Use Analytical Model │
                                                      └──────────────────────┘
┌──────────────────────┐
│ Do You Have Sufficient│
│ Resources and Available│
│ Data for Numerical     │──────────────────▶ Use Numerical Model
│ Models?                │
└──────────────────────┘
      No        Yes
```

several numerical solute fate and transport models (e.g., BIOPLUME III, RT3D, SEAM3D) have been developed or updated and revised to explicitly simulate the effects of petroleum hydrocarbon biodegradation via sequential electron acceptor processes for biodegradation in conjunction with previously developed algorithms for simulating advection, dispersion, and sorption.

4.3.3.1.1   Analytical Models

Analytical solutions provide exact, closed-form solutions to the governing advection-dispersion equation by making significant simplifying assumptions. The more closely the actual system approximates these assumptions, the more accurate the analytical model will be in predicting solute fate and transport. Analytical solutions are continuous in time and space and provide information on the temporal and spatial distribution of hydraulic head or solute concentrations for the governing initial and boundary conditions. The main advantage of analytical solutions is that they are simple to use and they provide a good first approximation of solute transport in relatively simple hydrogeologic settings. Analytical solutions are generally limited to steady, uniform flow or radial flow, and should not be used for ground-water flow or solute transport problems in strongly anisotropic or heterogeneous media. In some cases, such as where potential receptors are a great distance away, or where the aquifer is homogeneous and isotropic, the analytical solution may adequately describe contaminant fate and transport.

Because analytical models are used to estimate the impacts of contamination on a site given the qualifying assumptions used to develop the model, they are best utilized for order-of-magnitude results because a number of potentially important processes are treated in the model in an approximate manner, or are ignored completely. For example, analytical models may include terms describing a variety of chemical and hydrological processes, but usually are not capable of incorporating subsurface heterogeneity. Due to the nature of the simplifying assumptions, analytical models may overestimate the spread of contamination, which results in model predictions that are overly conservative. Note that model assumptions that are appropriately conservative may aid in the acceptance of MNA-based remedies because these assumptions will generally lead to an increased level of confidence that potential receptors will not be impacted by site contamination.

The analytical solutions of the advective-dispersive equation presented in Appendix D of the original protocol (AFCEE, 1995) continue to provide the basis for the majority of analytical solutions that are used to model natural attenuation of dissolved solutes. These solutions allow solute concentrations to be calculated as a function of time and distance from the source of contamination. Although analytical solutions can be implemented using commonly available spreadsheets or mathematical analysis applications (e.g., MathCAD$^{®}$), the most significant advances in the area of analytical solutions has been the development of various software codes and user interfaces that aid the environmental professional in applying, calibrating, comparing, and displaying the results of various analytical solutions with existing field data. The decision of whether to use a spreadsheet, mathematical analysis application, or natural attenuation-specific modeling code will depend on the needs, resources, and skills of the modeler. For example, use of spreadsheets offers the modeler the most flexibility in manipulating the method of data input and output, but also results in the highest level of initial effort to develop. Once developed, however, a spreadsheet-based solution can be used as a template for future sites where the same model assumptions apply. On the other hand, existing proprietary or public domain codes for simulating natural attenuation generally require little or no modification to apply to a given site, but may have additional costs for purchasing the software and training users on how to appropriately apply the software using available site data.

One example of a public domain model that has been developed to support an MNA evaluation for fuel hydrocarbons sites is the BIOSCREEN Natural Attenuation Decision Support System (USEPA, 1996a). BIOSCREEN was developed by AFCEE for two purposes:

1. To provide a screening model to evaluate if natural attenuation is a feasible remedial approach; and

2. To provide a simple user interface that implements the recommendations of the original protocol (AFCEE, 1995) in a way that can be understood by site stakeholders.

In performing these functions, BIOSCREEN assumes a uniform, 1-D ground-water velocity but does allow for up to three directions of dispersive contaminant transport via input of dispersivity values for one, two, or three directions. Sorption is simulated using a retardation factor, and biodegradation can be simulated using either first-order decay or an instantaneous reaction model that is based on an expressed assimilative capacity approach. Use of the instantaneous reaction model requires input of the observed difference in electron acceptor concentrations between an upgradient location and the plume interior. BIOSCREEN also allows for the simulation of source decay and/or a specification of the mass of soluble compound remaining in the source area. BIOSCREEN output can be viewed as concentration-versus-distance plots along the plume centerline, 3-D visual representations (2-D plan view contaminant distribution with contaminant concentration values plotted on the vertical axis), mass-balance data that provides an estimate of the mass of contaminant degraded by each electron acceptor process (instantaneous reaction model only), and a mass-flux calculator that can be used to determine the mass flux of contaminants through a user-specified portion of the plume.

Calibration of BIOSCREEN to field data can be performed for both the first-order and instantaneous reaction models, although the calibration approaches are slightly different. For either method, model calibration is based on a visual comparison of model-simulated and field-measured contaminant concentration data along the plume centerline when the plume has reached a stable or receding condition (USEPA, 1996a). For the first-order biodegradation model, the first-order degradation rate is adjusted until simulated contaminant concentrations match available site data for a given set of contaminant transport and sorption parameters. Note that estimating a first-order biodegradation rate with the steady-state solution offered in the BIOSCREEN (or any other) model to contaminant concentrations for a plume that is still expanding will generally result in an overestimation of the contaminant degradation rate. At sites where contaminant plumes have not reached stability (or insufficient data exists to demonstrate stability), a range of values of biodegradation rates taken from the literature, and/or site-specific field estimates (e.g., estimates using the tracer method), can be used with site-specific values for contaminant transport and sorption parameters to estimate the expected distance for the contaminant plume to reach stability. For the instantaneous reaction model, a two-step calibration process is recommended, as required. As described in Wiedemeier *et al*. (1999), the primary calibration step is to modify model dispersivity values within the range of values expected based on plume size, aquifer material, and aquifer heterogeneity. A potential second calibration step for the instantaneous model is to revisit the concentration inputs for electron acceptor/reaction endproducts to evaluate whether the values used in the model are representative of average source area (or plume area) concentrations. For additional information on the application of BIOSCREEN to site data, users of this protocol may wish to refer to USEPA (1996a) and GSI (1997).

A second example of a recently developed analytical model for assessment of natural attenuation is the NAS model (Chapelle *et al*., 2003), which uses site data to help the user

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calculate both the NAC and the biodegradation coefficients described in Section 4.2.2.1.6. Once site-specific degradation rates have been developed (either uniformly across the site, or as a function of electron acceptor condition), these site-specific degradation rates can be used with user-specified contaminant transport and sorption parameters to predict whether contaminant concentrations may be expected to exceed a user-specified regulatory concentration at downgradient points of concern. In the event that user-specified downgradient concentrations are exceeded, the NAS model provides the user with an estimate for how much of a reduction in source concentration would be required to achieve the user-specified contaminant concentration at a user-specified downgradient location. In addition, the NAS model also estimates how long it would take to observe this change at the downgradient (and intermediate) locations. This latter prediction is particularly important in terms of defining realistic expectations of when the effects of a particular source remediation technology may be expected to be observed in downgradient monitoring locations. Like BIOSCREEN, the NAS model also offers a method for estimating the timeframe for regulatory concentrations to be achieved in the source area, based on a user-specified contaminant source mass (or average concentration and total source area volume).

4.3.3.1.2   Numerical Models

Numerical models provide approximate solutions to the advection-dispersion equation, require fewer simplifying assumptions, and are capable of addressing more complicated problems. However, application of numerical models to a site requires significantly more data, effort (in terms of cost and labor), and their solutions are, by definition, inexact numerical approximations. Numerical models require input parameters similar to those used for analytical models, but the spatial distribution of the input parameters must be known to make the use of a numerical model warranted. Unlike analytical models, numerical models allow subsurface heterogenieties and varying aquifer parameters to be simulated if the requisite data are available. Note that analytical solutions are sometimes used to verify the accuracy of numerical solutions by applying both the exact analytical solution and the numerical solution to the same ground-water flow system and comparing the results.

Several well-documented and widely-accepted numerical models are available for modeling the fate and transport of fuel hydrocarbons dissolved in ground-water under the influences of advection, dispersion, sorption, and biodegradation. For example, the BIOPLUME III model (USEPA, 1998b), developed by AFCEE, is based upon the USGS 2-D solute transport model (method of characteristics) of Konikow and Bredehoeft (1978). BIOPLUME III simulates both aerobic and anaerobic biodegradation in addition to advection, dispersion, sorption, and ion exchange. BIOPLUME III simulates the biodegradation of organic contaminants under as many as five electron acceptor conditions (i.e., aerobic, nitrate-reducing, iron(III)-reducing, sulfate-reducing, and methanogenic), and can simulate the production of iron(II) if iron(III)-reducing conditions are included in a specific site model. The BIOPLUME III model allows simulation of biodegradation using first-order kinetics, an instantaneous reaction model, or Monod kinetics. For the first-order and Monod kinetics models, no electron acceptor information is needed, as contaminant degradation rates are calculated solely as a function of contaminant concentrations. For the instantaneous reaction model, electron acceptors concentrations are required input, and the principle of superposition is used to 'react' the hydrocarbon plume with the electron acceptor plume(s). The limitations imposed on the BIOPLUME III model are based on the assumptions inherent to the underlying flow model (i.e., method of characteristics approach) and the approaches used to simulate biodegradation. In terms of flow modeling, the method of characteristics inherently assumes that contaminant flow paths exist (i.e., contaminant transport is dominated by advection), vertical variations in head and concentration are negligible (e.g., 2-D

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transport), and the aquifer is homogeneous and isotropic with respect to longitudinal and transverse dispersivities. In terms of biodegradation, BIOPLUME III does not simulate selective (or competitive) biodegradation of individual contaminant species because the model was designed to simulate fate and transport of a single hydrocarbon substrate. In addition, the instantaneous reaction model is a simplification of the complex, biologically-mediated reactions that are known to occur in the subsurface.

Previously performed studies have shown that BIOPLUME II (the predecessor to BIOPLUME III) can be used to successfully support the MNA option at fuel-hydrocarbon-contaminated sites (Downey and Gier, 1991; Parsons, 1994a through 1994d; Parsons 1995a through 1995q; Wiedemeier *et al.*, 1993, 1994a, and 1994b), and users of this protocol may wish to review one or more of these site case studies to examine how BIOPLUME II was used.

Another option for using numerical modeling to simulate natural attenuation is to use the MT3D model (Zheng, 1990), which is based on the MODFLOW ground-water flow model (McDonald and Harbaugh, 1988), either alone or with various add-on packages available in the MT3DMS (Zheng and Wang, 1998), RT3D (Clement *et al.*, 1998), and SEAM3D (Waddill and Widdowson, 1998) models. Each of the MT3D platform-based models simulates contaminant transport in up to three dimensions, and can be used to explicitly simulate the effects of solute advection, dispersion, diffusion, sorption, and first-order degradation. The aforementioned 'add-on' models (MT3DMS, RT3D, and SEAM3D) each allow for simultaneous simulation of multiple contaminants. RT3D and SEAM3D offer the additional option of explicitly simulating electron acceptor utilization and reaction endproduct formation through a variety of models. RT3D reaction kinetics can be simulated at fuel-release sites using an instantaneous reaction model (similar to the approach offered in BIOPLUME III) and a dual-Monod kinetics model which provides kinetic limitations on hydrocarbon biodegradation based on simulated availability of electron acceptors. An example of the application of RT3D to Hill AFB is available from Lu *et al.* (1999). SEAM3D also uses a dual-Monod kinetics model for simulating electron acceptor availability limitations on hydrocarbon biodegradation. In the SEAM3D model, an additional feature is the presence of a reversible inhibition model that can be used to simulate the sequential electron acceptor utilization process that is typically observed in both the laboratory and field (see Figure 3.3 and associated discussion). The SEAM3D model also offers explicit simulation of an immobile LNAPL phase that can be placed at any location within the model domain and used to simulate contaminant dissolution (and corresponding source depletion) using a first-order, equilibrium-based model. An example of the application of SEAM3D to a jet-fuel release as part of the Natural Attenuation Study at Columbus AFB is presented in Brauner and Widdowson (2001).

4.3.3.2   Conducting an Exposure Pathways Analysis

After the rates of natural attenuation have been documented and predictions of the future extent and concentrations of the contaminant plume have been made (either with or without using a solute fate and transport model), the proponent of MNA should perform an exposure pathway analysis, as described in Section 2.3. This analysis includes identifying potential human and ecological receptors at points of exposure under current and future land and ground-water use scenarios. If a solute fate and transport model was used to develop future predictions on contaminant concentrations at potential receptor locations, the quantitative model results should be compared against site-specific regulatory requirements to quantitatively support the exposure pathways analysis. If reasonably conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. From

this information, the potential for impacts on human health and the environment from contamination present at the site can be estimated.

4.3.3.3   Model Documentation and Presentation of Results

Model documentation is a critical component of the modeling effort. If the reader of the final MNA evaluation report cannot determine how the model was set up and implemented, the model is of little use. At a minimum, an MNA evaluation report that includes a numerical model must include a discussion of how the CSM was developed, how and why the model(s) applied to the site were selected, a list of all simplifying assumptions, boundary and initial conditions used, a description of how model input parameters were determined (e.g., was a specific parameter measured, estimated, or assumed?), the process used to interpolate data spatially, how the model was calibrated, and what types of sensitivity/uncertainty analyses were performed. Appendix D of the original protocol (AFCEE, 1995) provides an example table of contents for an MNA evaluation report (including appropriate modeling sections), and Appendices E and F of the 1995 protocol present examples of MNA reports. In addition, Chapter 9 of Anderson and Woessner (1992) provides a comprehensive description of the major components that should comprise a comprehensive modeling report.

Presentation of model results generally serves two purposes. The first purpose of presenting model results is to convey to the reader that the calibrated model does indeed represent observed concentrations from field data. The second purpose of presenting model results is to illustrate how model predictions relate to physical site features (spatial relationship) and/or how this relationship may change over time (temporal relationship). Presentation of model results will likely consist of both tables and figures that summarize relevant information used to implement the selected models. In terms of presenting model results, the level of effort (and corresponding expense) of developing a presentation format for results should be in line with the complexity of the model applied to the site. For example, when using an analytical solution model to simulate contaminant concentrations along the centerline of a steady-state plume, development of relatively simple concentration-versus-distance plots that depict model simulation results (solid line) and observed contaminant concentrations (discrete points) provides a visual aide that can be used to illustrate that the model has been calibrated to existing site data. This plot could also be annotated with arrows indicating significant 'real-world' features such as the location of the source area, a downgradient property boundary, or a surface-water body that serves as a discharge point.

If applying a more complex 2-D or 3-D numerical transport model, superposition of modeling results (using shaded isoconcentration contours, for example) over site base maps that depict interpolated isoconcentration contours (using solid lines, for example) based on field data is one approach to illustrating model calibration. Having demonstrated model calibration, site base maps of physical features can then be used to illustrate future predictions of plume dynamics, including whether the contaminants are expected to reach a downgradient point of compliance, and the timeframe of when dissolved contaminant plume recession can be expected. Other methods of presenting the 'goodness-of-fit' for a calibrated model to field data include 1) cross plots of model predicted values versus field-measurement values with a 45-degree line used to evaluate 'goodness-of-fit' and 2) calculation of numerical measures of model calibration, such as the root mean square approach described by Zheng and Bennett (2002), among others. Examples of information that is useful to present in tabular format include a list of model input parameters (including variable name, value used in calibrated model, range of values tested as part of sensitivity analysis, and rationale for selecting simulated values) and a list of output parameters, such as expected maximum plume dimensions or the range of anticipated remediation

timeframes for various model scenarios. Although the discussion here provides some general guidance on what (and how) to present in terms of model calibration and prediction data, the breadth and type of data presentation will, to some extent, be a site-specific decision that should be based on supporting the site-specific exit strategy.

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SECTION 5

RECOMMENDED METHODS FOR DESIGNING AND OPTIMIZING MONITORING NETWORKS

Time and experience have shown that the recommendations provided in the original protocol (AFCEE, 1995) appropriately describe how to design simple and effective LTM plans for MNA performance monitoring at fuel-release sites. Based on this experience, the recommendations in the original protocol should be used to develop LTM programs for MNA at fuel-release sites. In cases where an existing or proposed LTM program seems excessive when compared to the recommendations of the original protocol, the information in this section provides guidance on how to optimize the LTM program to achieve the goals described in the original protocol. The authors anticipate that the information provided in this section will be most appropriate for optimizing the LTM program at sites where the existing monitoring well network is relatively large. For example, the optimization approaches described in this section may be helpful at sites where the current LTM program consists of regular sampling of a large number of wells that were installed for site characterization, but are not required for performance monitoring of MNA.

5.1   PURPOSE OF MONITORING PROGRAMS

Ground-water monitoring programs have two primary types of objectives (USEPA, 1994; Gibbons, 1994):

1. Evaluate the extent of contaminant migration (and related plume expansion), particularly if a potential exposure point for a susceptible receptor exists, and confirming impacts (or lack thereof) to downgradient receptors (*spatial objectives*); and

2. Evaluate long-term temporal trends in contaminant concentrations at one or more points within or outside of the remediation zone (*temporal objective*).

Assessment of spatial and temporal concentration data facilitates evaluation of the remedial measure performance. Additionally, related objectives that should be met by the performance monitoring program of an MNA remedy for a fuel-release site (USEPA, 1999a; AFCEE, 2000c) include:

1. Demonstrating that natural attenuation is occurring according to expectations and verifying progress toward attainment of cleanup objectives;

2. Detecting changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce or enhance the efficacy of natural attenuation processes;

3. Detecting the mobilization of any potentially undesirable elements (e.g., iron, manganese, arsenic) in the reduced geochemical environment created by the introduction of anthropogenic carbon, as described in Section 1.4;

4. Detecting new releases of contaminants to the environment that could create an unacceptable risk to receptors or impact the effectiveness of the natural attenuation remedy;

5. Demonstrating the efficacy of institutional controls that were put in place to protect potential receptors; and

6. Verifying progress toward attainment of cleanup objectives.

The relative success of any remediation system and its components (including the monitoring network) should be judged based on the degree to which it achieves the stated objectives of the system. Designing an effective ground-water monitoring program involves locating monitoring points and developing a site-specific strategy for ground-water sampling and analysis that maximizes the amount of relevant information that can be obtained while minimizing incremental costs. Relevant information is only that which is required to effectively address the monitoring program objectives.

5.2   USE OF DATA QUALITY OBJECTIVES IN DEVELOPING SITE-SPECIFIC MONITORING PLANS

Application of the DQO process described by the USEPA (2000), and discussed previously in Section 3.2.3 as part of pre-mobilization of site characterization activities, may help site managers plan to collect data of the correct type, quality, and quantity to support defensible site decisions and provide the basis for development of the performance monitoring plan. Use of the DQO process facilitates development of monitoring objectives that are clearly stated and accompanied by specific, quantifiable performance criteria, thereby enhancing the usefulness of the performance monitoring program. Two examples of qualitative DQOs/decision statements relevant to a performance monitoring program of an MNA remedy are:

1. Determine whether there are any changes in conditions that may adversely affect the efficacy of natural attenuation.

    a. Are there changes in ground-water flow rates and directions that would impact plume stability?

    b. Are there changes in the geochemical environment that would impact plume stability or contaminant reduction?

2. Determine whether there are any unacceptable impacts to receptors.

    a. Are there unacceptable impacts to surface water bodies, wetlands, or other ecological receptors?

    b. Are there impacts to water-supply wells, indoor air in adjacent buildings, or soil that could impact human receptors?

An example of how DQO #2 above can be made into a quantitative DQO is: "Determine, with greater than 95-percent confidence, that contaminant concentrations in ground water are not exceeding a health-based concentration standard within 500 feet of a water-supply well."

These types of decision statements and associated identification of data needs that address the decision statements are developed as the DQO process is implemented. The decision statements and data needs are used to develop the performance monitoring program for an MNA remedy. Regulatory acceptance of specific performance objectives is important; therefore, involving regulators in the development of these objectives is recommended.

5.3 DEVELOPMENT OF AN APPROPRIATE MONITORING PROGRAM

Designing an effective monitoring program involves 1) locating ground-water monitoring wells, 2) developing a site-specific ground-water sampling and analysis strategy, and 3) developing a site-specific contingency plan that includes specific "triggers" for contingency implementation. The monitoring program should be designed to monitor contaminant plume dynamics over time (i.e., Is the plume advancing, retreating, or steady-state?), and to verify that natural attenuation is occurring at rates sufficient to protect potential downgradient receptors and to attain site closure within an acceptable time frame.

The reader should refer to *Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation* (AFCEE, 2000c) for a detailed discussion of this topic. Key concepts discussed in the above-referenced document are briefly introduced and summarized in this section.

5.3.1 Monitoring Point Placement and Installation

In some cases, wells installed during site characterization may not be appropriate or necessary for LTM. Therefore, it is important to be selective in determining which of the existing wells to sample. It may be desirable or necessary to install one or more new wells at key locations purely to satisfy LTM objectives. A detailed understanding of the contaminant plume (e.g., lateral and vertical extent and distribution of concentrations throughout the plume) and site-specific hydrogeology (e.g., directions and velocities of ground-water and dissolved contaminant migration, presence of preferential migration pathways such as permeable sand layers) is required to ensure that LTM wells are screened in the same hydrogeologic unit as the contaminant plume and that they are in the path of contaminated ground-water flow.

Two types of wells, performance monitoring wells (PMWs) and contingency monitoring wells (CMWs), are used for LTM after the initial site characterization (Section 3) and baseline evaluation of natural attenuation (Section 4) (USEPA, 1998d). The PMWs, located upgradient from, within, and just downgradient from the plume, are used to verify the predictions made during the evaluation of natural attenuation. Periodic monitoring of cross-gradient PMWs also may be desirable at some sites to more fully define the plume boundary over time; these cross-gradient wells could be monitored relatively infrequently (e.g., biennially) if existing data indicate that the plume is not expanding in the cross-gradient direction, or is expanding relatively slowly. CMWs are placed beyond the maximum predicted lateral and downgradient boundaries of the plume, and typically upgradient from known or potential receptor exposure points, to ensure that the plume does not threaten human health or the environment (**Figure 5.1**). If pre-established trigger levels (defined during development of DQOs, Section 5.1) are exceeded at the CMWs, then a contingency plan should be implemented.

As described in detail in AFCEE (2000c), typical PMWs for a plume that does not discharge to a surface water body should be installed 1) upgradient (and possibly cross-gradient, as described above) from the plume in unimpacted ground water; 2) within the source area that is characterized by the presence of persistent LNAPL; 3) downgradient from the LNAPL source area, along the approximate longitudinal axis of the plume; and 4) downgradient from the plume in the dominant ground-water flow direction. In addition, one or more CMWs should be located as described in the previous paragraph.

For plumes that discharge to a surface water body, the PMWs downgradient from the plume should be replaced with surface water monitoring points within, upstream from, and downstream from the estimated plume discharge area to provide information on the impact of the contaminant

FIGURE 5.1

SCHEMATIC OF PERFORMANCE AND CONTINGENCY MONITORING WELL LOCATIONS

Extent of Dissolved Contaminant Plume

Extent of NAPL

Groundwater Flow Direction
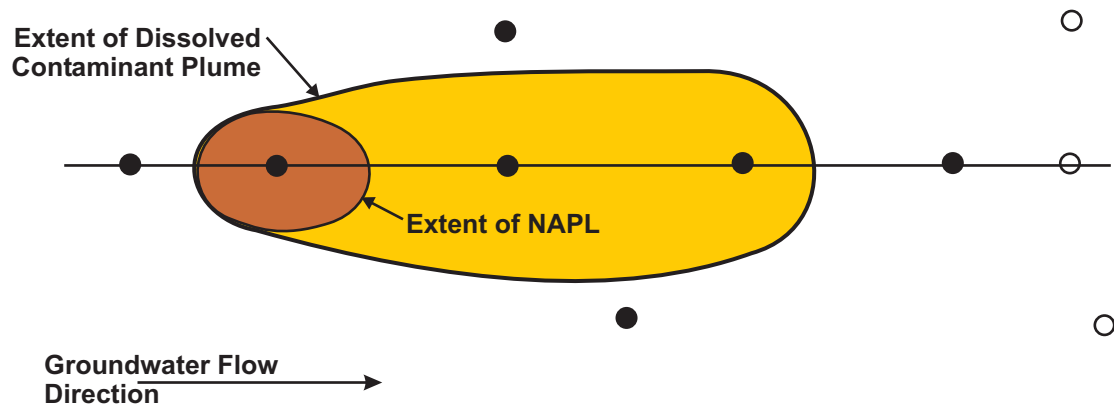
LEGEND

● Performance Monitoring Well

○ Contingency Monitoring Well

plume on the surface water body. In addition, if at least a portion of the plume flows beneath a surface water body, then installation of one or more wells on the downgradient (i.e., far) side of the surface water body is recommended.

5.3.2   Monitoring Event Frequency

According to the USEPA (1998d), the frequency of LTM should be related to:

- The natural variability in contaminant concentrations;
- The distance and travel time from the source to the location where acceptance criteria are applied; and
- The reduction in contaminant concentration required to meet the acceptance criteria.

Quarterly sampling of LTM wells during the first year of sampling may be useful to help confirm the direction of plume migration and to better establish baseline conditions and seasonal variability. If significant variability is encountered during the first year, then additional quarterly (or semiannual) sampling may be required. AFCEE (2000c) recommends that, based on the results of the first year of sampling, the sampling frequency may be reduced to annual (or less frequent) sampling in the quarter showing the highest contaminant concentrations or the greatest extent of the dissolved plume. USEPA (1999a) emphasizes that flexibility for adjusting the monitoring frequency over the life of the remedy should be included in the monitoring plan. For example, it is appropriate to decrease the monitoring frequency at fuel-release sites where it has been determined that natural attenuation is progressing as expected and there is little change observed from one sampling event to the next. In contrast, the monitoring frequency may need to be increased if unexpected conditions (e.g., plume expansion) are observed. The potential existence of regulatory requirements regarding the frequency of monitoring events should be considered and factored into site-specific plans as appropriate. Typical factors considered in developing an optimal monitoring frequency are summarized in **Table 5.1**.

TABLE 5.1
MONITORING FREQUENCY DECISION LOGIC

Reasons for a Relatively High Sampling Frequency (e.g., quarterly to semiannual)	**Reasons for a Relatively Low Sampling Frequency (e.g., annual to biennial)**
Ground-water velocity is high	Ground-water velocity is low
Change in contaminant concentration at a particular location would significantly alter a decision or course of action	Change in contaminant concentration at a particular location would not significantly alter a decision or course of action
Well is close to source area or operating remedial system	Well is distant from source area or remedial system
Insufficient historical data to predict if concentrations will change significantly over time	Concentrations are not expected to change significantly over time, or contaminant levels have been below ground-water cleanup objectives for a prescribed period of time

Perhaps the most critical factors to consider when developing a monitoring program are the distance to potential receptors and the seepage velocity of ground water and dissolved contaminants. Typically, the faster the ground-water/contaminant seepage velocity and the shorter the distance to potential receptor exposure points, the greater the sampling frequency. AFCEE (2000c) provides an example of how the appropriate sampling frequency could be determined for a hypothetical site based on the distance between the leading edge of the contaminant plume and a downgradient contingency well located in the plume's flowpath, and the seepage velocity of the ground water.

5.3.3   Parameter Measurement Frequency

The suggested TAL for LTM at fuel-release sites includes contaminants and geochemical parameters (see Section 3.4.3.4 for recommended sampling procedures). As described in Section 3.4.3.4.1, validation or baseline monitoring is performed for a limited number of sampling rounds following the initial site characterization to confirm site conditions and temporal variability. Validation monitoring consists of collecting the complete analytical suite specified in Table 3.3 (i.e., fuel-related contaminants depending on the type of fuel released, DO, nitrate, iron(II), sulfate, methane, temperature, pH, conductivity, alkalinity, and ORP). In contrast, LTM involves collecting a subset of the validation monitoring parameters. The subset selected for analysis on an ongoing basis will be site-specific; however, at a minimum it should include site-specific COCs, DO, ORP, temperature, and pH. Any federal or state-specific analytical requirements not discussed in Section 3.4.3 also should be addressed in the Sampling and Analysis Plan (SAP) to ensure that all data required for regulatory decision-making are collected. Geochemical parameters should be targeted for analysis based on the utility of the data for affecting site-related decisions. In other words, if measurement of a given geochemical parameter would not change the path to site closure or other site decisions, then measurement of that parameter should not be performed.

At a well-characterized site, the DQO process described in Section 5.2 can be used to choose parameters and measurement frequencies for each monitoring location based on the value of the data to evaluating MNA, as an alternative to the measurement of all parameters at all locations during every sampling event. For example, if results from several years of monitoring indicate that the geochemistry in the central portion of a BTEX plume is stable (and this is often the case), it may not be necessary or useful to continue to analyze samples from these locations for all of the geochemical indicator parameters during each sampling event.

Water-level measurements should be collected during each sampling event to monitor ground-water flow direction and gradient (vertical and horizontal). It may be desirable to measure water levels in a greater number of wells than are sampled for water quality because water level measurements are quick and inexpensive. In addition, collecting water level measurements at all serviceable monitoring wells provides the opportunity to periodically observe the physical condition of these wells.

5.4   OPTIMIZATION OF EXISTING MONITORING NETWORKS

AFCEE (2000c) states that, for sites where there are many years of defensible data demonstrating a stable or shrinking plume and site conditions are unlikely to change, the monitoring strategy can be optimized to focus on critical areas. This document also describes methods for evaluating plume stability and behavior that complement the information provided in this protocol.

AFCEE's (1997c) *Long-Term Monitoring Optimization Guide* provides general guidance on optimization of LTM networks for ground water, and is available on the remedial process optimization (RPO) webpage of the AFCEE's Environmental Restoration website (http://www.afcee.brooks.af.mil/products/rpo/default.asp). This guide was developed to provide instruction to project managers for the optimization of their LTM programs through the identification and application of appropriate strategies and optimization tools. The specific optimization strategies discussed in the guide include:

- Establishing decision rules for well placement and sampling frequency;

- Refining field procedures and analytical protocols; and

- Streamlining data management.

Most of the strategies that are introduced in AFCEE's LTM Optimization Guide, such as qualitative optimization evaluations and use of geostatistical tools, have been incorporated into LTM network optimization methodologies that can be applied by site managers and their contractors. Three of these methodologies are discussed below in Sections 5.4.1 through 5.4.3. The AFCEE (1997c) guide also provides a useful discussion of logic diagrams known as sampling frequency decision trees (SFDTs), which lead to a recommendation of the optimum sampling frequency for a specific well. An example SFDT also is provided in the AFCEE guide.

Three methodologies for optimizing larger monitoring networks that can be used to evaluate both sampling frequency and the number and location of sampling points are 1) MAROS developed for AFCEE by GSI, 2) a three-tiered approach developed for AFCEE by Parsons, and 3) a Geostatistical Temporal/Spatial (GTS) Optimization Algorithm developed by AFCEE. Text in the following subsections describes these three MNO methodologies in order of increasing complexity of use. A more detailed description of the three-tiered and MAROS techniques is provided in Appendix G of the *Remedial Process Optimization Handbook* (AFCEE, 2001b). In addition, the USEPA Technology Innovation Office recently published a study that compares the results of applying the three-tiered and MAROS approaches to monitoring data from three test sites (USEPA, 2004).

5.4.1   MAROS

MAROS is a relatively user-friendly collection of tools that have been bundled into one software package.   The tools include models, statistics, heuristic rules, and empirical relationships that assist the user in optimizing a ground-water monitoring network while maintaining adequate delineation of the plume and knowledge of plume dynamics over time. In general, the MAROS method applies to two-dimensional aquifers that have relatively simple hydrogeology. However, for a multi-aquifer (three-dimensional) system, the user could apply the statistical analysis layer by layer. Ground-water monitoring data can be imported from Microsoft Excel® spreadsheets, Microsoft Access® database tables, or entered manually.

In MAROS 2.0, two levels of analysis are used for optimizing LTM plans: 1) an overview statistical evaluation with interpretive trend analysis based on definition of temporal trends and plume stability and 2) a more detailed statistical optimization based on spatial and temporal redundancy reduction methods. It should be noted that the standard and recommended practice for evaluating statistical analyses for relative importance of a well location/sample frequency, such as those offered by MAROS, is to perform a qualitative optimization evaluation (i.e., a "reality check") of recommendations that are based primarily on statistical analyses for spatial importance. The purpose of performing this reality check is to assess whether there are other issues or factors that are not adequately accounted for by the statistical analysis. As an example,

a pure statistical evaluation for spatial coverage of a monitoring well network may assign a high degree of spatial importance to a monitoring well located distant and cross-gradient from a contaminant plume simply due to an absence of other wells in the area. However, historical monitoring of the ground-water flow direction and COC concentration data may indicate that this well is so far removed from the contaminant flow path that it is highly unlikely that ground-water contaminants will ever migrate anywhere near this particular well. In this case, the qualitative reality check evaluation is used to assess whether the wells recommended for retention in the monitoring program by MAROS are located appropriately to monitor plume dynamics, or if one or more of these wells have been retained simply because they are located in an area having a relatively low well density.

The specific analysis tools contained in MAROS that enable performance of the overview and detailed statistical evaluations are briefly summarized in the following subsections. A detailed description of the structure of the MAROS software and utilities can be found in the MAROS 2.0 User's Manual (AFCEE, 2002), which can be downloaded along with the software from www.gsi-net.com. Additional information on the role of qualitative reality checks in the MNO process is provided in Section 5.4.2 and USEPA (2004).

5.4.1.1   Overview Statistics: Plume Trend Analysis

The Overview Statistics are designed to facilitate a better understanding of plume behavior over time and how well-specific concentration trends are spatially distributed within the plume. This step allows the user to gain information that will support a more informed decision to be made in subsequent detailed statistics analysis. The Overview Statistics package contains the following tests or routines:

- Mann-Kendall Analysis: A non-parametric statistical procedure (Mann, 1945; Kendall, 1975; Gilbert, 1987) that is well suited for analyzing trends in data over time. The concentration trend is classified by MAROS into one of six categories, including decreasing, probably decreasing, stable, no trend, probably increasing, and increasing.

- Linear Regression Analysis: A parametric statistical procedure that is typically used for analyzing trends in data over time. Concentration trends are classified into one of the six categories listed above for the MK test.

- Overall Plume Analysis: Provides preliminary monitoring system optimization recommendations for each COC that consist of: 1) minimum number of wells that should be sampled, 2) minimum sampling frequency, and 3) the estimated sampling duration (in years). The Overall Plume Analysis routine uses simple decision rules that are based on trend analysis results and site-specific information (provided by the user) to develop optimization recommendations. MAROS also offers the option to analyze the monitoring network on a well-by-well basis using a more rigorous statistical approach. This more rigorous statistical approach is described in Section 5.4.1.2 and AFCEE (2002).

- Moment Analysis: Provides a relative measure of plume stability and condition, and can be used to assist the user in evaluating the impact on plume delineation of removing existing wells from the LTM program. A trend analysis of the results of the moment analysis provides insight into temporal changes in dissolved mass, center of mass location, and plume spreading. Note that the MAROS software developers are currently in the process of fixing several programming errors that have been discovered in the MAROS method-of-moments calculations. A corrected version of MAROS is

scheduled for release during the fall of 2004. MAROS users who are planning to use method-of-moments calculations to evaluate plume dynamics should ensure that they are using the corrected version of MAROS prior to attempting to interpret and publish the results of a Moment Analysis.

5.4.1.2   Detailed Statistics: Optimization Analysis

In addition to the general recommendations provided on sampling frequency and density by the Overview Plume Analysis component of MAROS described in Section 5.4.1.1, MAROS also offers a more detailed analysis that performs evaluation of sampling frequency, well redundancy, well sufficiency, and sampling sufficiency on a well-by-well basis. The MAROS Detailed Statistics module allows for a quantitative analysis for spatial and temporal optimization of the well network on a well-by-well basis. The Detailed Statistics module can be used to determine the minimum number of sampling locations, and the lowest frequency of sampling, that can still meet the spatial and temporal objectives of the existing monitoring program. This module also provides a statistical assessment of the confidence that the network of wells used to collect concentration data for each individual historical monitoring event has been sufficient to conclude that a user-specified compliance concentration was or was not exceeded at a user-specified compliance boundary. The specific tools used in the Detailed Statistics evaluation include:

- Well redundancy and sufficiency analyses using the Delaunay triangulation method (Aziz *et al.*, 2002);

- Sampling frequency determination using the Modified Cost Effective Sampling method (Ridley and MacQueen, 1998); and

- Data sufficiency analysis using statistical power analyses.

5.4.2   Three-Tiered Approach

The three-tiered approach developed by Parsons for AFCEE has been applied at numerous sites to date. Although a formal user's guide for the three-tiered methodology has not been developed, the aforementioned USEPA (2004) report comparing the results of the three-tiered and MAROS approaches provides a description and examples of how to apply the three-tiered approach to site-specific monitoring data. It should be noted that use of this approach requires the services of 1) an environmental professional with substantial experience in site characterization and ground-water monitoring to perform the qualitative evaluation and 2) a scientist with the ability to perform spatial statistical analysis of environmental data. The temporal analysis does not require specialized skills and can be performed by most environmental professionals with access to the proper software. In addition, the three-tiered approach requires the use of standard, commercially available statistical and geostatistical software (e.g., Geostatistical Analyst™ software package developed by the Environmental Systems Research Institute, Inc [ESRI], 2001) This approach combines the following tiers of analysis:

- A qualitative evaluation (i.e., using professional judgment by an experienced practitioner) that considers factors such as hydrostratigraphy, locations of potential receptors with respect to the dissolved plume, and the direction(s) and rate(s) of contaminant migration to establish the frequency at which monitoring should be conducted, and if each well should be retained in or removed from the monitoring program. Example decision logic that can be used to perform the qualitative evaluation is summarized in **Table 5.2.**

TABLE 5.2
MONITORING NETWORK OPTIMIZATION DECISION LOGIC

Reasons for Retaining a Well in a Monitoring Network	Reasons for Removing a Well from a Monitoring Network
Well is needed to further characterize the site or monitor changes in contaminant concentrations through time	Well provides spatially redundant information with a neighboring well (e.g., same constituents, same water-bearing zone, and/or short distance between wells)
Well is important for defining the lateral or vertical extent of contaminants	Well has been dry for more than 2 years[a]
Well is needed to monitor water quality at a compliance or receptor exposure point (e.g., domestic well)	Contaminant concentrations are consistently below laboratory detection limits or cleanup goals
Well is important for defining background water quality	

a/ Water-level measurements in dry wells should continue, and sampling should be re-evaluated if the well becomes re-wetted.

- An MK statistical analysis to determine the temporal trends of COCs over time, and application of an algorithm to determine the relevance of the trends within the monitoring network. A flow chart of the decision logic applied to the temporal trend analysis results is presented in **Figure 5.2.**

- A determination of the relative amount of spatial information contributed by each monitoring well via performance of a spatial geostatistical analysis. Application of geostatistical methods to the results of the ground-water monitoring program at a given site can be used to estimate COC concentrations at every point within the dissolved contaminant plume, and also to generate estimates of the "error," or uncertainty, associated with each estimated concentration value. Thus, the monitoring program can be "optimized" by using available information to identify those areas having the greatest uncertainty associated with the estimated plume extent and configuration. Sampling points can be successively eliminated from simulations, and the resulting uncertainty examined, to evaluate if significant loss of information (represented by increasing error or uncertainty in estimated chemical concentrations) occurs as the number of sampling locations is reduced. Repeated application of geostatistical estimating techniques, using tentatively identified sampling locations, then can be used to generate a sampling program that would provide an acceptable level of certainty regarding the distribution of COCs with the minimum possible number of samples collected. Furthermore, application of geostatistical methods can provide unbiased representations of the distribution of COCs at different locations in the subsurface, enabling the extent of COCs to be evaluated more precisely.

After each of the three analysis tiers listed above is completed, the results of the three analyses are combined to establish the frequency at which monitoring should be conducted, as well as the optimal number and locations of wells in the monitoring network. A primary advantage of the three-tiered methodology is that it incorporates both qualitative and statistical

**FIGURE 5.2
TEMPORAL TREND DECISION RATIONALE FLOW CHART**
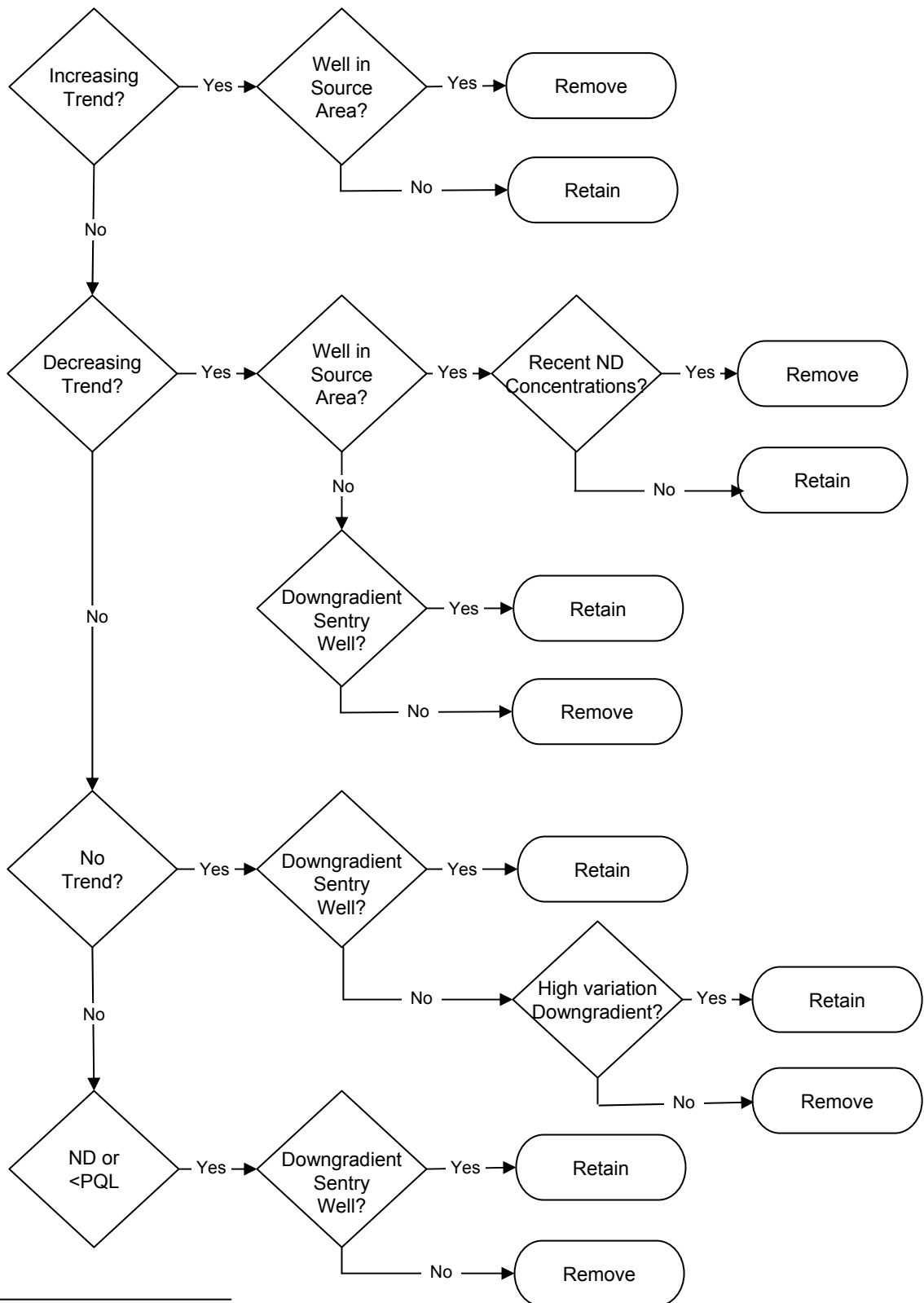
Notes

ND = not detected
PQL = practical quantitation limit

S:\ES\Remed\TO24\NA Studies\14000 – FuelsProtocol\Figures\Figure5.2.ppt

evaluations in a structured package that defines how the results of the various evaluations should be combined and used.

5.4.3   GTS Optimization Algorithm

GTS is similar to MAROS and the three-tiered technique described above in that it is a site-specific technique (i.e., the optimized solution is unique to the site). The GTS approach incorporates a greater variety of statistical tests than the three-tiered approach; therefore, application of this method may provide a greater amount of information that can be used to make MNO-related decisions. However, a limitation of the GTS approach is that this procedure requires a larger database for initial application than either MAROS or the three-tiered approach. GTS would typically be applied at sites that have 40 or more monitoring wells with sufficient sampling data over time and space. Time-series data should span at least 4 quarters to account for seasonality, and sample sizes should ideally exceed 8 events per well. Application of the GTS algorithm requires an expert geostatistician along with standard, commercially available, statistical and geostatistical software. Depending on site complexities and the number of sampling locations, the labor to perform the expert geostatistical analysis using GTS can take approximately one man-month. Files describing the algorithm are available for download on the RPO page of the AFCEE website (http://www.afcee.brooks.af.mil/products/rpo/default.asp). The two optimization algorithms contained within the GTS package are described in the following subsections.

5.4.3.1   Temporal Optimization Algorithm

The GTS temporal algorithm is divided into two components: 1) computation of a composite temporal variogram and 2) "iterative thinning" of sampling events at selected wells. The purpose of the variogram construction is to measure the average correlation between pairs of measurements as the time lag between them increases or decreases. For example, samples taken from the same location at shorter intervals will tend to be correlated to some degree, and therefore are at least partially redundant in the statistical information that they provide. Using the variogram, an average optimal sampling frequency for adoption on a site-wide basis can be identified.

"Iterative thinning" refers to the temporary removal of randomly-selected data points from the time series of measurements at a given well. If the data set trend (estimated using Sen's method [Sen, 1968; Gilbert, 1987]) is still close to the original trend, then additional thinning can occur until the "thinned" trend estimate is significantly different from the original trend. If the trend of the thinned data set is not significantly different, then temporally redundant data exist and the sampling frequency can be adjusted to further lengthen the time between sampling events.

5.4.3.2   Spatial Optimization Algorithm

The spatial optimization algorithm employed in the GTS technique is very similar to that used in the three-tiered approach (Section 5.4.2). The algorithm is predicated on the notion that well locations are redundant if nearby wells offer nearly the same information about the plume. A well is considered redundant if its removal does not significantly change an interpolated map of the plume (i.e., no significant changes in the locations of isoconcentration contours). An initial plume map is generated via kriging, and wells are then iteratively removed from the data set; the degree to which the spatial uncertainty increases as a result of the removal is then assessed. In this way, wells that provide the least amount of spatial information can be identified and considered for removal from the monitoring program.

5.4.4 Summary of Current Technical Resources

The following publications provide useful guidance regarding developing and/or optimizing monitoring programs for fuel-release sites undergoing natural attenuation. In most cases, the primary relevant concepts presented in these documents have been introduced in this protocol; however, the user may want to refer to the source documents for additional details.

Developing Data Quality Objectives

Data Quality Objectives Process for Hazardous Waste Site Investigations QA/G-4HW Final (USEPA, 2000). Provides general, nonmandatory guidance on developing DQOs for environmental data collection operations in support of hazardous waste investigations. Application of the DQO Process will help site RPMs plan to collect data of the right type, quality, and quantity to support defensible site decisions.

Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives (ASTM, 1995i). Covers the process of development of DQOs for the acquisition of environmental data. The guidance presented in this document is compatible with the guidance presented in the USEPA (2000) DQO document referenced above.

Clarifying DQO Terminology Usage to Support Modernization of Site Cleanup Practice (USEPA, 2001d). The intent of this document is to provide, in a brief and unambiguous manner, a basic conceptual understanding of DQO-related terms in a way that facilitates systematic project planning in the context of site cleanups.

Air Force Remedial Process Optimization Field Procedures and Quality Assurance Handbook, Version 2.0 (AFCEE, 1999c). This document describes the field procedures and QA aspects of RPO, and is designed to be used in conjunction with the AFCEE RPO Handbook (AFCEE, 2001b). The document summarizes key USEPA guidance and provides links to full text sources when available. USAF-specific QA requirements also are summarized. Use of the USEPA's DQO process is also discussed.

Developing and Optimizing Ground-Water Monitoring Programs

Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation (AFCEE, 2000b). This document describes how to effectively and efficiently specify the location, frequency, and types of samples and analyses required to meet the objectives of validation monitoring and LTM. In addition, guidance is provided on developing contingency remedies that will not adversely impact the natural biodegradation reactions occurring at a site, should engineered approaches be required.

Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites (USEPA, 1999a). The purpose of this Directive is to clarify USEPA's policy regarding the use of MNA for the remediation of contaminated soil and ground water in the Superfund, RCRA Corrective Action, and Underground Storage Tank programs. The Directive contains specific guidance on performance monitoring to evaluate remedy effectiveness.

Monitoring and Assessment of in-situ Biocontainment of Petroleum Contaminated Ground-Water Plumes (USEPA, 1998d). This document describes an approach for the collection and evaluation of soil and ground-water monitoring data for determining the efficacy of *in situ* biocontainment and to identify "stabilized" fuel-impacted ground-water plumes.

Monitoring and Remediation Optimization System (MAROS) Software User's Guide. (AFCEE, 2002). This reference is for the beta Version 2.0 software package. The software is described in Section 5.4.2 of this document, and may be downloaded from www.gsi-net.com.

Optimization of LTM Networks Using GTS: Statistical Approaches to Spatial and Temporal Redundancy (Cameron and Hunter, 2000). This reference consists of a series of three files available that provide details on the optimization approach described in Section 5.4.3 of this protocol. These documents are available for download on the RPO webpage of AFCEE's Environmental Restoration website (http://www.afcee.brooks.af.mil/products/rpo/default.asp).

Final Long-Term Monitoring Optimization Guide, Version 1.1 (AFCEE, 1997c). This guide was prepared to assist DoD installation managers in the optimization of their LTM programs by identifying and applying the appropriate strategies and optimization tools.

SECTION 6

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IMPLEMENTING MONITORED NATURAL ATTENUATION AND EXPEDITING CLOSURE AT FUEL-RELEASE SITES

APPENDICES

Prepared for

**Air Force Center for Environmental Excellence
and
Defense Logistics Agency**

AUGUST 2004

APPENDIX A

**CONTAMINANTS OF POTENTIAL CONCERN
AND
THEIR MOVEMENT AND FATE IN THE ENVIRONMENT**

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A.0   INTRODUCTION

This appendix presents an overview of the factors affecting the fate and transport of fuels in the environment. Contaminant fate and transport is controlled by many factors, including a compound's physical and chemical properties, the presence or absence of other compounds, and the nature of the media through which the compound is migrating. The movement of contaminants must be understood on a site-specific basis to evaluate feasible remedial options and exposure to potential receptors.

A.1   COMPOSITION OF COMMON PETROLEUM FUELS

The production of petroleum distillate fuels involves vaporizing and recondensing crude petroleum. Crude oil, a degradation product of organic material (e.g., prehistoric animal and plant matter) is a complex mixture primarily composed of hydrocarbons, which are compounds consisting solely of carbon and hydrogen. Measured by weight, carbon and hydrogen represent at least 95 percent of the elements present in crude oil (Neumann *et al*., 1981). In comparison, hydrocarbon concentrations in refined petroleum products such as gasoline, diesel fuel, and kerosene are even higher than in crude oil, because non-hydrocarbon compounds (which contain sulfur, nitrogen, oxygen, or trace metals) are destroyed or removed during the refining process (Owen and Corey, 1990). The chemical and physical properties of fuels will depend on the method by which the fuel was refined and/or blended, the nature of the crude oil feedstock, and the intended market (on-road versus off-road) (Stout *et al*., 2002).

In terms of individual compounds, the American Petroleum Institute (API) suggests that any given petroleum based fuel may contain several hundred compounds (API, 1994). Griest *et al*. (1985), the California Department of Health Services (California DHS, 1988) and the TPH Criteria Working Group (1998) have conducted extensive reviews of the chemistry of petroleum-based fuels. These studies suggest that, while there may be some variation in the hydrocarbon composition of distillate fuels within distinct boiling-point ranges, the differences are ordinarily not large because the fuels must meet American Society for Testing and Materials (ASTM) standards.

As a class, hydrocarbons have a wide range of physiochemical characteristics with wide ranges in molecular weight and boiling point. They can be very fluid or very viscous, volatile or nonvolatile, soluble or insoluble. This variability in physical and chemical character causes the behavior of individual hydrocarbons in the subsurface to vary greatly (Reisinger, 1995). The number of carbon atoms present in a hydrocarbon compound has a major effect on its properties (Nyer and Skladany, 1989). For all classes of hydrocarbons, aqueous solubility decreases, and the tendency of the hydrocarbon compound to sorb to soil particles (or "partition" to soil) increases, as the number of carbon atoms and compound molecular weight increase (API, 1994; Nyer and Skladany, 1989).

A.1.1   Hydrocarbon Structure

The carbon and hydrogen atoms in petroleum fuels are arranged into an almost infinite number of discrete molecules. These molecules are classified as alkanes, alkenes, and Aromatic

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hydrocarbons, on the basis of their structure (**Figure A.1**). Petroleum fuels may also contain other constituents added to enhance octane ratings, inhibit corrosion, or improve evaporation and condensation characteristics of the fuel.

Alkanes (or paraffins), are the major constituents of crude oil and usually the major constituents of refined petroleum products. Alkanes contain only carbon-carbon single bonds, and are subdivided into linear alkanes ("normal" alkanes), branched alkanes (isoalkanes), and naphthenes (cycloalkanes). Saturated hydrocarbon compounds, including the normal alkanes, comprise about 75 percent of the mass of a typical petroleum fuel (Griest *et al.*, 1985; Heath *et al.*, 1993; API, 1994). Alkane chains up to 17 carbon atoms in length are liquids, with densities less than water. Pure alkane compounds, composed of chains of 18 or more carbon atoms in length, are solids at room temperature, and are commonly referred to as waxes. Alkane solubility rapidly decreases as the number of carbon atoms in the compound increases. Vapor pressures also decrease as alkane carbon numbers increase. Alkenes (or olefins), are not usually constituents of crude oil, but are formed during the refining process. Alkenes contain one or more carbon-carbon double bonds, and may be found as linear, branched or cyclic molecules. Alkenes make up a limited fraction of gasolines, and are not usually a significant component of higher-boiling-point products, including diesel fuel.

Alkanes and alkenes from hexane (6 carbon atoms in a chain, or C_6) through dodecane (C_{12}) are most abundant in low-boiling-range petroleum distillates (e.g., gasoline). The alkanes from dodecane through octadecane (C_{18}) are most abundant in mid-range distillate fuels (e.g., diesel and fuel oil) (API, 1994).

Aromatic hydrocarbon compounds are based on the benzene ring structure, with conjugated carbon-carbon double bonds that produce chemical properties in aromatic hydrocarbons that are markedly different from other fuel components (**Figure A.2**). The aromatic compounds benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are the primary volatile constituents of petroleum-distillate fuels, and are relatively soluble in water when compared with most alkanes and alkenes. BTEX compounds in fuels are an environmental concern because they are relatively toxic and soluble (California DHS, 1988). The most abundant non-BTEX aromatic hydrocarbons in petroleum-based fuels include trimethylbenzenes (TMBs), tetralins/indans, tetramethylbenzenes (TeMBs), naphthalene, methylnaphthalenes, dimethylnaphthalenes, methyl-phenanthrenes, and dimethylphenanthrenes (Heath *et al*., 1993; API, 1994).

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile compounds (SVOCs) containing two or more benzene-ring structures, are generally less soluble, sorb to soil more strongly, have lower soil and water diffusions coefficients, and are therefore less mobile in the environment than monoaromatic compounds.

A.1.2   Fuel Types

The distillation process yields a series of fractions or "cuts" with characteristic distillation temperatures. It is possible to classify distillate fuels by their predominant carbon-atom ranges:

- Gasoline - C_4 to C_{12} hydrocarbons;
- Kerosene and jet fuels - C_{11} to C_{13} hydrocarbons;

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FIGURE A.1
TYPICAL STRUCTURES OF FUEL HYDROCARBONS

ALKANES

n- Alkane Structure

$C_5 H_{12}$
(n-Pentane)
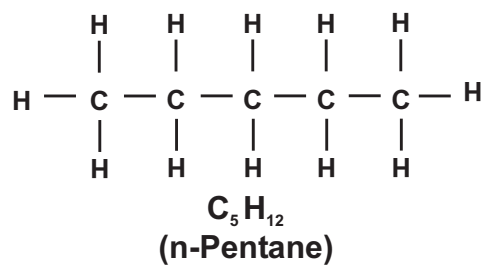
Isoalkane Structure

$C_5 H_{12}$
(2-Methlybutane)
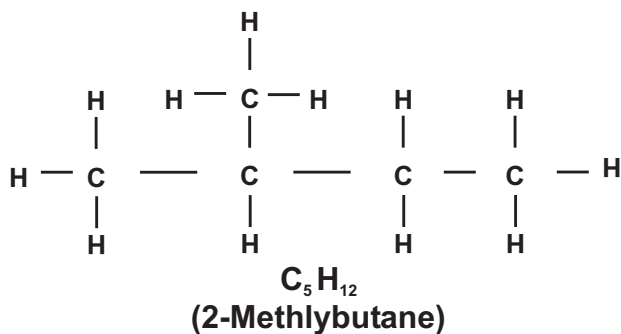
Cycloalkane Structure

$C_6 H_{12}$
(Cyclohexane)

AROMATICS

Single-Ring

$C_6 H_6$
(Benzene)

Two-Ring

$C_{10} H_8$
(Naphthalene)

Three-Ring

$C_{14} H_{10}$
(Phenanthrene)

ALKENES

$C_2 H_4$
(Ethylene)

S\draw\729691b rev.cdr ma 090203
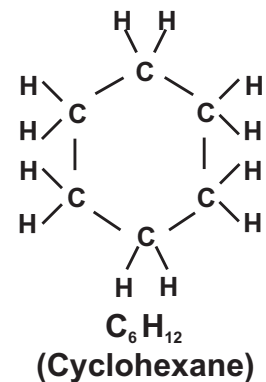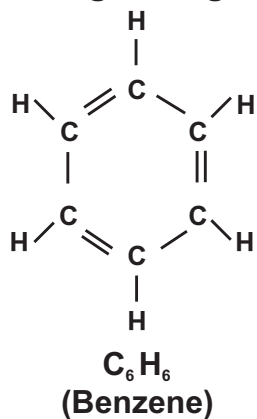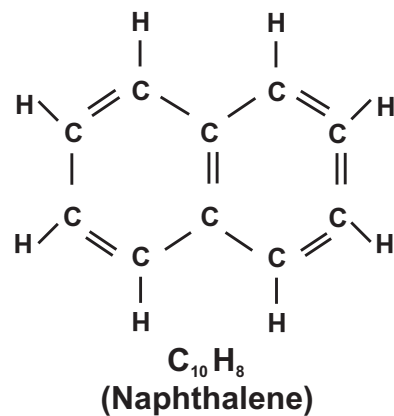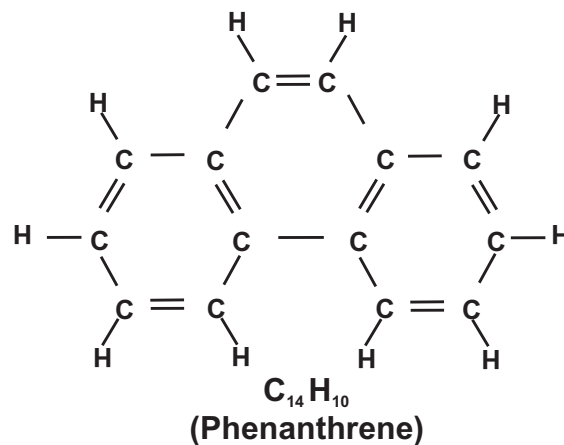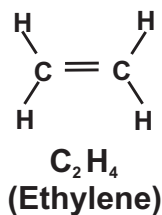
FIGURE A.2
TYPICAL STRUCTURES OF BTEX COMPOUNDS
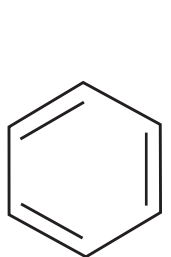
Benzene
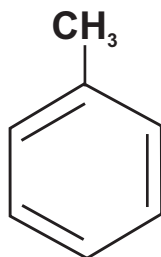
Toluene
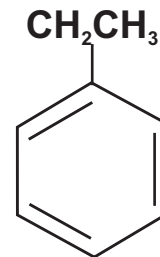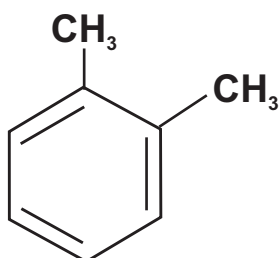
Ethylbenzene

ortho-Xylene
(1,2-Dimethylbenzene)
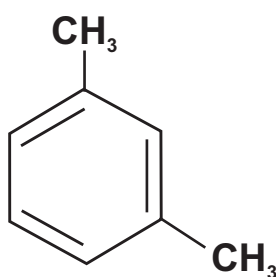
meta-Xylene
(1,3-Dimethylbenzene)
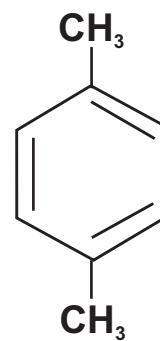
para-Xylene
(1,4-Dimethylbenzene)

- Diesel fuel and light fuel oils - C_{10} to C_{20} hydrocarbons;

- Heavy fuel oils - C_{19} to C_{25} hydrocarbons; and

- Motor oils and other lubricating oils - C_{20} to C_{45} hydrocarbons.

As the number of carbon atoms increases, there is an increase in the boiling point. The lighter, more volatile compounds are used directly in gasoline-range materials, and include substances with boiling points that are between –40°C and 220°C. The hydrocarbons in gasoline are typically in the C_4 to C_{12} range (Nakles *et al.*, 1996). Most gasoline blends are complex solutions containing 50 to 150 components formulated for burn rate (octane number), volatility (for consistent performance in hot and cold weather), and emission control (oxygenated fuels). Manufacturers commonly add aromatic hydrocarbons to gasoline to increase the octane rating, and typical premium gasoline formulation can contain up to 45 percent aromatic hydrocarbons (Cole, 1992). Typical percentages for various compounds in premium unleaded gasolines are listed in **Table A.1**.

<div align="center">

TABLE A.1
TYPICAL PERCENTAGES OF SELECTED COMPOUNDS
IN PREMIUM UNLEADED GASOLINES

</div>

Constituent	Super Unleaded (percent)
n-hexane	12.9
n- and 1-pentane	6.1
2-pentane	2.4
2-methyl pentane	4.3
iso-octane	8.7
Benzene	4.5
Toluene	7.1
Ethylbenzene	1.7
Xylenes	8.2
Methanol	9.0-11.0
All other	33.1-35.1

Diesel fuel, kerosene, and fuel oils consist of hydrocarbons in the boiling-point range between 175°C and 325°C (Smith *et al.*, 1981; Nyer and Skladany, 1989). These mixtures are generally less soluble and mobile than gasoline fuels. Diesel fuel encompasses the range of compounds from C_{10} to C_{19}, and is available in three grades based on volatility, ignition quality, viscosity and other characteristics. Kerosenes have commonly been used for heating fuel and jet fuel. Jet fuels commonly used by the United States Air Force (USAF) and United States Navy (USN) can generally be separated into two categories: "wide-cut" fuels and "kerosene-based" fuels (Martel, 1987). JP-4 is created by taking a "wide cut" of the distillate to include both the gasoline and kerosene fractions. JP-4 typically is composed of approximately 50 to 60 percent gasoline-range hydrocarbons and 40 to 50 percent kerosene-range hydrocarbons (Martel, 1987). This large percentage of gasoline imparts increased volatility to JP-4. By contrast, JP-5 and JP-8 are kerosene-based fuels that contain relatively less volatile, longer-chain hydrocarbons (Agency for Toxic Substances and Disease Registry [ATSDR], 1996a; Mayfield, 1996). The main grades of commercial jet fuel are Jet A-1 and Jet A. A less common commercial jet fuel (Jet B) is a blend of gasoline and kerosene that is rarely used except in very cold climates due to it's relatively high flammability. Methanol/water mixtures may be added to jet fuels to increase the aircraft's take-off power.

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Lubricating oils contain heavy-end hydrocarbons (C_{20} to C_{45}) and are made from the more viscous portion of the crude oil that remains after removal of lighter fractions. Lubricating oils may contain up to 30 percent additives including pour point depressants, viscosity index improvers, defoamers, oxidation inhibitors, antiwear compounds, and friction-reducing compounds.

Waste oil is a common contaminant at fuel-release sites. PAHs formed in the combustion chambers of internal combustion engines are concentrated in the motor oil, and are commonly in the 10 to 20 mg/kg range, compared to PAH levels in new lubricating oil that are often near the range of detectability (around 0.3 mg/kg). In addition to hydrocarbons, waste oils commonly contain other contaminants such as metals, chlorinated compounds, and polychlorinated biphenyls (PCBs).

The majority of states have established cleanup standards for total petroleum hydrocarbons (TPH), total extractable petroleum hydrocarbons (TEPH) and/or total volatile petroleum hydrocarbons (TVPH), and the analysis required is typically related to the type of fuel released (Appendix B). There is some variation between states and laboratories on the method names, carbon ranges, and boiling ranges for these analyses. In addition, the term TVPH may be used interchangeably with gasoline-range organics (GRO), and TEPH may be used interchangeably with diesel-range organics (DRO). A typical carbon range for analysis of TVPH-GRO is C_6 to $C_{12,}$ and a typical carbon range for TEPH-DRO is C_{10} to C_{28} (Severn-Trent Laboratories, 2003). The TPH/TVPH/TEPH parameters are commonly used because they provide a simple and economical method of evaluating the extent of contamination and include the majority of the chemicals in petroleum hydrocarbon compounds. However, there are limitations to the use of TPH (and TEPH/TVPH) because different analytical methods may yield different results, and similar TPH values may represent different chemical compositions and toxicities (Sigal *et al.*, 1997).

A.1.3 Fuel Additives

Fuel additives are commonly used to increase octane ratings and reduce air pollution. Since the early 1920s, tetra ethyl lead [$Pb(CH_2CH_3)_4$] and tetra methyl lead [$(CH_3)_4Pb$] have been blended with gasoline to increase it's octane rating. The addition of lead results in the formation of lead and lead oxide particles during combustion, causing the fuel to burn more slowly and smoothly. The use of leaded gasoline resulted in high lead levels in the air, dust, and soil near roadways. In 1996, the Clean Air Act (CAA) banned the sale of leaded fuel for on-road vehicles, however the United States Environmental Protection Agency (USEPA) has continued to allow leaded fuel to be sold for off-road uses, including aircraft, racing cars, farm equipment, and marine engines. Other additives associated with leaded gasoline include ethylene dichloride (EDC) and ethylene dibromide (EDB).

In 1990, amendments to the CAA required areas in violation of the national ambient air quality standards to use oxygenated gasoline. Commonly-used oxygenate additives include methyl tert-butyl ether (MtBE), ethanol, and methanol. In 1995, the USEPA implemented the Reformulated Gasoline (RFG) Program to address air quality issues in ozone non-attainment areas.

The fuel oxygenate MtBE ($C_5H_{12}O$) was first used as an octane-enhancing replacement for lead in the 1970s (USEPA, 2003). MtBE is a flammable liquid with a distinctive, sweet odor that is made from blending chemicals such as isobutylene and methanol. MtBE is designed to reduce carbon monoxide and ozone emissions, as well as to boost octane ratings. In some RFG areas of the country, MtBE is substituted for ethanol in the summer months to reduce the tendency of volatile fuels to evaporate (Parsons, 1999).

Typically, gasoline may contain up to 15 percent MtBE by volume (USEPA, 2003). In a survey of community water supplies (CWS) conducted by the United States Geological Survey (USGS), MtBE was detected in 14 percent of surface-water sources, 5 percent of ground water sources, 4 percent of CWS serving 10,000 people or less, and 15 percent of CWSs serving 10,000 people or more (Hirsch, 2001). Recent legislation in some states has called for the elimination of MtBE from gasoline due to the presence of this compound in private and public drinking water supplies. In 2000, the USEPA recommended phasing out MtBE as a fuel-oxygenate, and has begun taking steps to ban the use of MtBE as a gasoline oxygenate. MtBE is a highly soluble and polar molecule, sorbs poorly to soil and is therefore mobile once dissolved in ground water.

To comply with CAA requirements for carbon monoxide and ozone, use of ethanol and methanol as gasoline oxygenates (as a substitute for MtBE) has been increasing. Ethanol is essentially 100-percent pure alcohol produced by fermenting plant sugars, and can be made from corn, potatoes, wood, waste paper, brewery waste, other agricultural products, and food wastes. Various formulations of RFG blend ethanol and/or methanol with gasoline to reduce carbon monoxide emissions. Ethanol has been used as a gasoline additive for many years as a 10 percent mixture in a blend called "gasohol". More recently, fuels such as E85 (ethanol blended with 15 percent gasoline), E95 (ethanol blended with 5 percent gasoline), and E93 (ethanol blended with 5 percent methanol and 2 percent kerosene) are more being used in isolated locations around the nation. In the US, methanol has also been used as fuel alternative for flexible-fuel vehicles that run on M85 (85 percent methanol and 15 percent gasoline), although use of M85 is declining because automakers no longer are supplying methanol-powered vehicles. Ethanol and methonal are completely miscible in water, sorb poorly to soil, and are therefore very mobile in ground water.

A.1.4   Inorganic Compounds

Inorganic compounds may be present at fuel-impacted sites at concentrations that present a potential threat to human health and the environment, particularly if waste oils were part of the petroleum release. Note that these types of contaminants are site-specific, and are highly dependent on the type of fuel releases, and in the case of arsenic, naturally-occurring chemistry of soil and ground water. Arsenic has been identified as a contaminant of potential concern (COPC) in limited parts of the nation where natural arsenic concentrations in aquifer and/or bedrock materials are known to occur. The concern of arsenic mobilization following a fuel release is that, under the reducing geochemical conditions typically encountered within a contaminant plume, solid-phase arsenic may be reduced, solubilized, and subsequently transported downgradient as part of the dissolved contaminant plume. The decision on whether to include for arsenic as a COPC should be based on knowledge of the chemical composition of soil and bedrock formations that are likely to be impacted by a dissolved contaminant plume of fuel constituents.

A.2 HEALTH CONCERNS OF COMMON CONTAMINANTS OF POTENTIAL CONCERN AT FUEL-RELEASE SITES

Exposure to gasoline, diesel, and/or fuel oil vapors can have adverse effects on human health [American Conference of Governmental Industrial Hygienists (ACGIH), 2003]. For example, breathing diesel fuel vapors for long periods may cause kidney damage and lower the blood's ability to clot. The International Agency for Research on Cancer (IARC) has determined that some heavy fuel oils may cause cancer in humans, but there is not enough information for the lighter fuels to make a determination (ASTDR, 1996b). In addition, exposure to jet fuel vapors has been shown to cause nausea, headaches, coordination (or other central nervous system) problems, and fatigue (ATSDR, 1996b and 1999).

Contaminants of concern (COCs) are defined as specific chemicals that pose a risk to human health and the environment and require remediation to meet state or federal regulatory standards. Although COCs will vary between fuel-impacted sites, the primary COCs at fuel-impacted sites (e.g., fuel hydrocarbons and fuel additives) are summarized in **Table A.2**. Although metals, total volatile organic compounds (VOCs), or PCBs have not been listed in Table A.2, these contaminants are typically associated with releases of waste oil and should be considered as part of the COPC list at waste oil release locations. BTEX compounds have various potential health effects (as listed in Table A.2). Federal maximum contaminant levels (MCLs) have been established for BTEX in drinking water (Table 1.1 of Section 1.4), and almost every state has established cleanup standards for BTEX compounds in soil and ground water at fuel-impacted sites (Appendix B). For PAHs, the Department of Human Health and Services (DHHS) has determined that several PAHs are expected carcinogens (ATSDR, 1996c). A federal MCL has been established for benzo(a)pyrene in drinking water, and over half the states have established cleanup standards for one or more PAH compounds in soil and ground water at fuel-impacted sites. Note that the primary components of most fuels (i.e., alkanes and alkenes) are virtually non-toxic, and are generally considered immobile because these compounds are nearly insoluble in water (Zemo *et al.*, 1995).

Health concerns and, in some cases, regulatory standards exist for many fuel additives, including MtBE, lead, EDB, EDC, ethanol, and methanol. For MtBE, acute toxicity to exposed animals and humans is expected to be low, but questions have been raised concerning the potential human risk of developing cancer from long-term exposure to MtBE and/or its metabolites (Williams and Sheehan, 2002). DHHS, IARC, and USEPA have not classified MtBE as to its carcinogenicity (ATSDR, 1997). Currently, USEPA has not established an MCL for MtBE, but a secondary (aesthetic-based) standard is expected in the near future (Williams and Sheehan, 2002). In advance of promulgating an actual standard, USEPA has issued an advisory guidance level for MtBE of 20 to 40 μg/L based on taste and odor considerations. The USEPA issues advisories to provide guidance for drinking-water contaminants for which there are no national regulations. According to USEPA, the advisory level is about 20,000 to 100,000 (or more) times lower than the range of exposure levels in which cancer or noncancer effects were observed in rodent tests (USEPA, 1997). Some states have established primary (health-based) or secondary standards for MtBE in drinking water (Appendix B). For example, California has set a primary MCL of 13 μg/L and a secondary standard of 5 μg/L. MtBE ground water cleanup levels for each state can be found on USEPA's website (www.epa.gov/swerust1/mtbe).

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TABLE A.2
PRIMARY CONTAMINANTS OF CONCERN AT FUEL-RELEASE SITES

Potential COCs	Fuel Released	Human Health Effects
Benzene	Gasoline Diesel	Cancer[a]
Ethylene dichloride (EDC)	Gasoline	Liver, narcosis [a]
Ethylbenzene	Gasoline Diesel	Irritation, central nervous system [a]
Ethylene dibromide (EDB)	Gasoline	Irritation, liver, kidney [a]
Lead	Gasoline Jet fuel	Central nervous system, gastrointestinal, blood, kidney, reproductive [a]
MtBE	Gasoline	Irritation, kidney, reproductive [a]
Naphthalene	Jet fuel Diesel Waste oil	Irritation, ocular, blood [a]
Polynuclear aromatic hydrocarbons (PAHs)	Jet fuel Diesel Waste oil	Some PAHs are reasonably expected to cause cancer [b]
Toluene	Gasoline Diesel	Central nervous system [a]
Total petroleum hydrocarbons	All fuel sites	Varies
Xylene isomers	Gasoline	Irritation, blood [a]

[a] ACGIS, 2003
[b] ATSDR, 1996c

In terms of the other former or current fuel additives, cleanup standards for lead, EDB, and/or EDC have been established by some, but not all, states (Appendix B). Although ACGIH (2003) indicates a concern that ethanol could be a human carcinogen if exposure occurs over long periods of time and USEPA (2001) notes that methanol is of concern because a few teaspoons can cause blindness and a few tablespoons can be fatal, a review of available literature did not identify any cleanup standards for methanol or ethanol.

A.3   PHASE PARTITIONING OF FUELS

Petroleum hydrocarbon fuels may exist in the environment in any of following four different phases (see also Section C.2 of Appendix C):

- Pure light non-aqueous phase liquid (LNAPL),

- Part of an aqueous solution dissolved in water,

- Solid phase (sorbed to, or occluded between, soil particles); or

- Vapor.

The degree to which a particular chemical is segregated among these phases is known as partitioning. Under specified conditions of temperature, pressure, and moisture content, in a particular soil matrix, each compound will partition between ground water, soil, and soil vapor, with the direction of phase transfer driven toward equilibrium.

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Subsurface transport of petroleum hydrocarbons is driven by potential gradients – gravitational, hydraulic, or chemical. In the unsaturated zone, volatilized compounds move in response to chemical concentration gradients. If the relative vapor density of the volatile phase is greater than that of air, some chemical migration in the vapor phase may be downward (Mallon, 1989). In general, however, vapor-phase migration is from the subsurface to the atmosphere. The transport of volatilized compounds in the unsaturated zone depends on the permeability of the soil, the soil moisture content, ambient air temperature, and barometric pressure. Below the water table, there are no continuous air-filled pores, and vapor-phase transport does not occur.

In most situations, LNAPLs will migrate downward through the soil in the unsaturated zone, and compounds with a high affinity for the matrix through which they are migrating will sorb to the matrix or partition into native organic carbon (Reisinger, 1995). Highly soluble hydrocarbons will tend to dissolve in vadose zone water. If the volume of hydrocarbon exceeds the residual capacity of the vadose zone soils, it will migrate downward until it reaches a low permeability zone or the capillary fringe. LNAPL that reaches the capillary fringe will spread until sufficient pressure (LNAPL head) develops to enable the liquid to penetrate the capillary fringe and migrate to the water table. At that point, the various constituents of the LNAPL begin to dissolve in ground water, in accordance with their relative solubilities (Mallon, 1989).

The density of most refined petroleum products is less than the density of water, and the solubilities of most of the constituents of refined petroleum products are relatively low (API, 1994). As a consequence, some of the petroleum LNAPL will not dissolve into ground water, and cannot migrate as a dissolved constituent below the water table. Rather, a petroleum fuel that migrates to the water table will generally spread laterally from the initial point of introduction as an immiscible phase at the air-water interface. Seasonal or other fluctuations in the elevation of the water table produce a "smear zone" of residual petroleum product in direct contact with ground water. Because the more-soluble constituents of the petroleum LNAPL gradually dissolve from the LNAPL into ground water, the "smear zone" can function for some extended period of time as a source of contaminants in ground water. After fuel constituents have been dissolved in water, aqueous-phase transport can occur in the unsaturated and the saturated zones.

As water from the ground surface percolates through contaminated soil in the unsaturated zone, chemicals present as LNAPL, sorbed to the soil matrix, or as a vapor can be dissolved and migrate with the infiltrating water to the water table. The transport rate of dissolved constituents in the unsaturated zone depends on the permeability of the soil, its water content, and the concentrations of dissolved chemicals in percolating water. If contaminated water evaporates into the atmosphere, most of the dissolved constituents are left in the environmental medium (e.g., water body, soil at land surface) from which evaporation occurs. However, some constituents remain at low concentrations in the water vapor, and are thus transferred to the atmosphere in the vapor phase (Hem, 1989; Driscoll, 1986).

A.4 CHEMICAL PROPERTIES AND PROCESSES THAT AFFECT CONTAMINANT FATE AND TRANSPORT

Contaminant fate and transport is controlled by the physical and chemical properties of the contaminant and the nature of the subsurface media through which the contaminant is migrating.

Important chemical properties that influence contaminant fate and transport include vapor pressure, Henry's Law constant (H), solubility, soil partition coefficient (K_d), organic carbon/water partition coefficient (K_{oc}), and octanol/water partition coefficient (K_{ow}). **Table A.3** includes common fuel compounds and chemical properties that influence their fate and transport. Additional information on chemical and physical properties of various compounds can be obtained from the USEPA webpage located at www.epa.gov/oppt/exposure/docs/episuitedl.htm or by downloading a free software program called EPISUITE. This program includes such information as vapor pressure, boiling points, Henry's Law constants, and solubility and will estimate these properties based on chemical structure if there are no data in its database.

The following site-specific conditions also influence the fate and migration of contaminants.

- Hydraulic conductivity,

- Porosity,

- Total organic carbon content,

- Precipitation,

- Grain size distribution,

- Ground water geochemistry, and

- Indigenous bacterial populations.

The major processes affecting chemicals in the subsurface include volatilization, sorption to soil, advection, diffusion, and chemical and biological degradation (Nyer and Skladany, 1989). These processes are summarized in **Table A.4**. Those processes that result only in the reduction of a contaminant's concentration but not of the total contaminant mass in the system are termed nondestructive and include dispersion, diffusion, sorption, volatilization, and dilution. Those processes that result in a reduction in the total mass of contaminant in the system are referred to as destructive. Biodegradation is the dominant destructive attenuation mechanism acting on fuel compounds. A literature search did not identify any documents providing evidence of abiotic destruction of fuel compounds.

A.4.1   Volatilization

Volatilization is the process by which a constituent is converted from a solid or liquid phase to vapor, ultimately resulting in transfer of the chemical to the atmosphere. The volatility of a particular chemical is a function of that chemical's vapor pressure and Henry's Law constant. The vapor pressure of a substance at a reference temperature is the pressure exerted by the vapor phase of the substance in equilibrium with the liquid or solid phase of the substance, at that temperature. A chemical with a high vapor pressure has a greater tendency to volatilize to the atmosphere than does a chemical with a low vapor pressure. The Henry's Law constant is a measure of the relative tendency of a chemical to move between the dissolved phase and vapor phase, and is a function of the vapor pressure and solubility of the chemical. A chemical with a high Henry's Law constant will have a high ratio of chemical concentration in the vapor phase compared with that chemical's concentration in the dissolved phase, and will be more likely to volatilize to the surrounding atmosphere.

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TABLE A.3
PROPERTIES OF SELECTED COMPOUNDS

Compound	Molecular Weight (g/mol)[a]	Henry's Law Constant (atm-m³/mol)[b]	Vapor Pressure (mm Hg @ 20°C)[c]	Density (g/cm³)[d]	Solubility (mg/L)[e]	Vapor-Air Diffusion Coefficient (cm²/day)[f]	Water-Liquid Diffusion Coefficient (cm²/day)	K$_{oc}$ (mL/g)[g]
Aromatic Hydrocarbons								
Benzene	78.11 [h]	5.43E-03 [i]	7.60E+01 [j]	0.877 [h]	1,780 [j]	7,980 [k]	0.94 [l]	9.12E+01 [j]
Toluene	92.14 [h]	5.94E-03 [i]	2.20E+01 [j]	0.867 [h]	515 [j]	7,344 [l]	0.82 [l]	1.51E+02 [m]
Ethylbenzene	106.17 [h]	8.44E-03 [n]	7.00E+00 [j]	0.867 [h]	152 [j]	6,566 [l]	0.78 [l]	2.57E+02 [m]
o-Xylene	106.17 [h]	5.10E-03 [i]	5.00E+00 [j]	0.880 [h]	175 [j]	6,307 [l]	0.61 [l]	1.29E+02 [m]
m-Xylene	106.17 [h]	7.68E-03 [i]	6.00E+00 [j]	0.864 [h]	146 [i]	5,962 [l]	0.61 [l]	1.59E+02 [m]
p-Xylene	106.17 [h]	7.68E-03 [i]	6.50E+00 [j]	0.861 [h]	198 [j]	5,789 [l]	0.61 [l]	2.04E+02 [m]
1,2,4 Trimethyl benzene	120.19 [h]	5.70E-03 [o]	2.03E+00 [o]	0.862 [h]	51.9 [p]	5,924 [p]	0.60 [p]	3.72E+03 [o]
n-Propyl benzene	120.19 [h]	1.08E-02 [o]	2.50E+00 [j]	0.862 [h]	60.24 [o]	5,560 [k]	0.53 [k]	7.41E+02 [o]
n-Butyl benzene	134.22 [h]	1.25E-02 [o]	1.03E+00 [q]	0.860 [h]	12.8 [p]	5,740 [p]	0.58 [p]	2.51E+03 [o]
s-Butyl benzene	134.22 [h]	1.14E-02 [o]	1.10E+00 [j]	0.862 [h]	11.8 [o]	5,220 [o]	0.50 [o]	8.91E+02 [o]
t-Butyl benzene	134.22 [h]	1.17E-02 [o]	1.50E+00 [j]	0.867 [h]	18.0 [o]	5,220 [k]	0.50 [k]	6.76E+02 [o]
n-Pentyl benzene	148.25 [h]	6.73E-02 [r]	3.62E-01 [q]	0.859 [h]	1.05 [p]	5,468 [p]	0.55 [p]	4.90E+04 [p]
n-Hexyl Benzene	162.27 [h]	2.16E-02 [r]	1.03E-01 [q]	1.063 [h]	1.02 [p]	5,232 [p]	0.52 [p]	2.04E+05 [p]
Polycyclic Aromatic Hydrocarbons								
Acenaphthene	154.21 [h]	1.90E-04	1.55E-03 [m]	1.024 [h]	3.93 [m]	5,184 [l]	0.52 [l]	5.10E+03 [k]
Anthracene	178.23 [h]	8.60E-05 [s]	1.70E-05 [s]	1.283 [h]	0.045 [s]	4,666 [l]	0.49 [l]	1.40E+04 [s]
Benzo(a)anthracene	228.29 [h]	1.00E-06 [s]	2.20E-08 [s]	1.274 [h]	0.0057 [s]	4,640 [k]	0.44 [k]	2.00E+05 [s]
Benzo(b)fluoranthene	252.32 [h]	1.20E-05 [m]	5.00E-07 [m]	not provided	0.014 [m]	3,801 [l]	0.42 [k]	5.50E+05 [m]
Benzo(k)fluoranthene	252.32 [h]	3.87E-05 [s]	5.00E-07 [s]	not provided	0.00043 [k]	4,450 [k]	0.42 [k]	5.50E+05 [s]
Benzo(ghi)perylene	276.00 [j]	1.21E-07 [s]	1.03E-10 [s]	not provided	0.00026 [j]	4,350 [k]	0.41 [k]	1.60E+06 [s]
Benzo(a)pyrene	252.32 [h]	4.90E-07 [s]	5.60E-09 [s]	1.351 [m]	0.003 [j]	3,974 [l]	0.43 [k]	5.50E+06 [s]
Chrysene	228.29 [h]	1.05E-06 [s]	6.90E-09 [s]	1.274 [h]	0.006 [j]	3,974 [l]	0.44 [k]	2.00E+05 [s]
Dibenzo(a,h)anthracene	278.36 [o]	1.70E-06 [o]	2.78E-12 [o]	1.282 [o]	0.00249 [o]	3,950 [l]	0.40 [k]	1.65E+06 [o]
Dibenzofuran	168.19 [h]	5.82E-05 [o]	2.63E-03	1.089 [h]	10 [j]	5,570 [k]	0.55 [k]	1.00E+04 [m]
Fluoranthene	202.26 [h]	6.50E-06 [s]	5.00E-06 [s]	1.252 [h]	0.265 [j]	4,233 [l]	0.48 [k]	3.80E+04 [s]
Fluorene	166.22 [h]	2.10E-04 [m]	7.10E-04 [m]	1.203 [h]	1.9 [j]	4,750 [l]	0.52 [k]	5.00E+03 [m]
Indeno(1,2,3,cd)pyrene	276.34 [j]	6.95E-08 [s]	1.00E-10 [s]	not provided	0.062 [s]	4,320 [k]	0.41 [k]	1.60E+06 [s]
Napthalene	128.17 [h]	4.60E-04 [m]	7.10E-02 [m]	1.025 [h]	30 [j]	6,110 [k]	0.60 [k]	1.30E+03 [m]
1-Methyl naphthalene	142.20 [p]	4.40E-04 [t]	4.20E-02 [l]	1.020 [h]	28.4 [p]	6,048 [l]	0.54 [l]	3.57E+03 [t]
1,3 Dimethyl naphthalene	156.20 [p]	1.96E-03 [p]	7.61E-02 [p]	1.014 [h]	8 [p]	5,417 [p]	0.54 [p]	1.26E+04 [p]
2,6 Dimethyl naphthalene	156.20 [p]	1.54E-04 [p]	1.50E-03 [p]	1.003 [t]	2 [p]	5,185 [p]	0.52 [p]	9.77E+03 [p]
1,4,5 Trimethyl naphthalene	176.20 [p]	2.25E-04 [p]	2.03E-03 [p]	1.009 [h]	2.1 [p]	5,185 [p]	0.52 [p]	3.80E+04 [p]
Phenanthrene	178.23 [h]	2.26E-04 [s]	9.60E-04 [s]	0.980 [h]	0.816 [j]	4,650 [l]	0.51 [k]	1.40E+04 [s]
1-Methyl phenanthrene	192.30 [p]	7.16E-02 [p]	7.61E-02 [u]	not provided	0.269 [p]	4,889 [p]	0.48 [p]	3.36E+04 [o]
Pyrene	202.26 [h]	5.10E-06 [s]	6.87E-07 [s]	1.271 [h]	0.135 [s]	4,406 [l]	0.48 [k]	3.80E+04 [s]
Gasoline Additives								
Lead	207.20 [h]	1.00E-50	5.31E-26	11.340 [h]	0.01 [v]	3,650 [k]	2.06 [k]	>1,000 (K$_d$[w])
Methyl-tert-butyl ether	88.15 [h]	5.87E-04	2.49E+02	0.741 [h]	43,000-54,300[x]	6,770 [k]	0.66 [k]	1.12E+01
Ethanol	46.07 [h]	2.50E-04	2.30E-04	0.816	miscible	not provided	not provided	0.00E+00
EDB (1,2 Dibromoethane)	187.86 [o]	2.50E-03 [o]	1.10E+01 [o]	2.168 [o]	4,200 [o]	not provided	not provided	4.37E+01 [o]
EDC (1,2 DCA)	98.96 [o]	1.11E-03 [o]	8.70E+01 [o]	1.235 [o]	8,300 [o]	7,680 [k]	0.79 [k]	1.90E+01 [o]

[a] g/mol = grams per mole

[b] atm-m³/mol = atmosphere-cubic meter per mole

[c] mm Hg = millimeters of mercury

°C = degrees Celsius

[d] g/cm³ = grams per cubic centimeter

[e] mg/L = milligrams per lier

[f] cm²/day = square centimeters per day

[g] mL/g = milliliters per gram

[h] Weast et al., 1989.

[i] Howard et al., 1990a.

[j] Verschueren, 1983.

[k] estimated using Lyman et al., 1990.

[l] Tetra Tech, Inc., 1988.

[m] Montgomery and Welkom, 1990.

[n] Howard et al., 1990b.

[o] Montgomery, 1996.

[p] API, 1994.

[q] Weast and Grasselii, 1989.

[r] Ceazon et al, 1989.

[s] Atlantic Environmental Services, Inc., 1988.

[t] Calabrese and Kostecki, 1993.

[u] Dragun, 1988.

[v] Hem, 1976.

[w] Battelle, 1984.

[x] API, 2000.

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TABLE A.4
SUMMARY OF IMPORTANT PROCESSES ACTING ON COMPOUNDS IN THE SUBSURFACE

Process	Description	Dependencies	Possible Effects
Advection	Movement of solute by bulk ground-water movement.	Dependent on aquifer properties, mainly hydraulic conductivity, effective porosity, and hydraulic gradient. Independent of contaminant properties.	At most sites, provides the main mechanism driving contaminant movement in the subsurface.
Dispersion	Fluid mixing due to ground-water movement and aquifer heterogeneities.	Dependent on aquifer properties and scale of observation. Independent of contaminant.	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration.
Diffusion	Spreading and dilution of contaminant due to molecular diffusion.	Dependent on contaminant properties and concentration gradients. Described by Fick's Laws.	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant at most ground-water flow velocities.
Sorption	Reaction between aquifer matrix and solute whereby the relatively hydrophobic compounds become sorbed to organic carbon or clay minerals.	Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity, octanol-water partitioning coefficient).	Tends to reduce solute transport rate and remove solutes from the ground water via sorption to the aquifer matrix.
Infiltration	Infiltration of water from the surface into the subsurface.	Dependent on aquifer matrix properties, depth to ground water, and climate.	Dilution of the contaminant plume, replenishes electron acceptor concentrations, especially dissolved oxygen. Sorbed compounds may also be dissolved into infiltrating water.
Volatilization	Volatilization from LNAPL in saturated or unsaturated zones into the vapor phase in soil gas.	Dependent on the chemical's vapor pressure and Henry's Law constant.	Causes removal of solid- or liquid-phase compounds from the subsurface.
Biodegradation	Microbially mediated redox reactions.	Dependent on ground-water geochemistry, microbial population, and contaminant properties.	Most important process in contaminant mass reduction.
Dissolution from LNAPL to ground water	Partitioning from LNAPL into ground water. LNAPL plumes tend to act as a continuing source of ground-water contamination.	Dependent on aquifer matrix (relative permeability, capillary pressure, and residual saturation) and contaminant properties (solubility, mass fraction, volatility, density, interfacial tension).	Primary source of ground-water contamination.

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In many circumstances, low-molecular-weight compounds will volatilize in the vadose-zone and diffuse upward in soil gas. Included in this category are VOCs, alkanes up through dodecane, and aromatic compounds through naphthalene (API, 1994). The rates of volatilization of different hydrocarbons are directly proportional to their vapor pressures. Due to relatively high Henry's Law constant and vapor pressure, BTEX compounds are likely to be in the vapor phase. MtBE has a relatively low Henry's Law constant compared to BTEX, and is less likely to volatilize from the dissolved phase when compared to monoaromative hydrocarbon compounds. PAHs have relatively low Henry's Law constants and vapor pressures, and are considered SVOCs.

Volatilization is an important mechanism in removing VOCs from the unsaturated environment near the land surface. However, once a chemical has been dissolved in ground water, its potential for volatilization from the saturated zone in the subsurface is limited because vapor transfer across the capillary fringe can be very slow (McCarthy and Johnson, 1992). Chiang *et al*. (1989) demonstrated that less than 5 percent of the mass of dissolved BTEX is lost to volatilization in the saturated ground water environment. Rivett (1995) observed that, for dissolved-phase plumes deeper than about one meter below the air/water interface, only low chemical concentrations would be detectable in soil vapor due to the downward movement of ground water near the water table. This suggests that very little, if any, chemical mass will be lost to volatilization in areas in which chemicals occur in ground water at depths greater than a few feet below the water table.

A.4.2   Solubility and Mass Transport of Solutes

Dissolved constituents can enter the unsaturated zone via infiltration of water that contains chemicals dissolved from an above-ground surface source, or the constituents can become dissolved as percolating water passes through a source of constituents in soil. The aqueous solubility of a chemical species provides an indication of how readily that particular compound could dissolve into ground water. The factors that influence how these dissolved contaminants move through porous media include advection, dispersion, diffusion, and retardation.

A.4.2.1   Solubility

Solubility is defined as the ability or tendency of one substance to blend uniformly with another. Chemicals with higher aqueous solubilities will tend to dissolve into the aqueous phase, and to migrate through soil, transported by infiltrating vadose-zone water, or in ground water.

BTEX compounds are moderately soluble, as a consequence of their molecular structure. The aqueous solubility of the BTEX compounds ranges from 1,780 milligrams per liter (mg/L) for benzene to 146 mg/L for *m*-xylene. The solubility of MtBE is in the range of 50,000 mg/L, and ethanol is completely miscible. PAHs range from moderately soluble to virtually insoluble in water. Chemicals with low solubilities will become sorbed or occluded in soil, and are unlikely to migrate with infiltrating vadose-zone water or in ground water.

Constituents having moderate to high solubilities typically are the most mobile in the subsurface because they are most likely to be available for transport in the aqueous phase. The less-soluble chemicals become adsorbed or occluded in soil, and are unlikely to migrate appreciable distances in the aqueous phase. The solubility of neat MtBE (approximately 50,000

mg/L) is more than one order of magnitude greater than that of benzene (1,780 mg/L). The partitioning of MtBE and benzene between an oil mixture (gasoline) and water is affected in part by the solubility of the two compounds in water. At a particular temperature, the solubility of a pure organic liquid is a constant (e.g., the values reported for solubility in Table A.4). However, the solubility of a compound is reduced when other organic compounds are present in the liquid organic phase (e.g., gasoline). The result is that the equilibrium aqueous solubility of component species dissolving from a mixture will be:

$$S_i^{\ e} = \gamma_i \cdot X_i \cdot S_i^{\ w} \qquad\qquad (A-1)$$

where:

$S_i^{\ e}$ =   effective solubility of component i [M/L^3];

γ_i =   activity coefficient of species i in a mixture (usually very close to 1.0);

X_i =   mole fraction of component i in the mixture (mole/mole); and

$S_i^{\ w}$ =   pure-phase aqueous solubility of component i [M/L^3].

For a compound having a molecular weight similar to the mean molecular weight of the mixture [~100 grams per mole (g/mol) for gasoline], X_i is closely approximated by the compositional fraction of the component on a weight or volume basis (Squillace *et al.*, 1997).

The high aqueous solubility of MtBE, together with its high concentrations in oxygenated gasoline, can produce elevated concentrations of MtBE in water contaminated by gasoline spills. For a gasoline that is 10 percent by weight MtBE, X_i for MtBE will be about 0.1. Assuming no depletion of the MtBE in the gasoline resulting from dissolution into water, and a pure-phase aqueous solubility of 50,000 mg/L, the concentration of MtBE in water in contact with gasoline could be as high as 5,000 mg/L. For comparison, the maximum concentration of benzene in water in contact with gasoline might be about 50 mg/L (assuming benzene comprises 3 percent of a gasoline by weight [California DHS, 1988]), and the total aqueous solubility of all hydrocarbons in a non-oxygenated gasoline is generally about 120 mg/L (Poulsen *et al.*, 1992).

Elevated concentrations of MtBE detected in ground water near underground storage tank (UST) spill sites are consistent with calculated gasoline/water partitioning (Squillace *et al.*, 1997). MtBE concentrations in the hundreds of mg/L have been reported for ground water samples (Davidson, 1995; Buxton *et al.*, 1997). These concentrations are not as high (thousands of mg/L) as might be expected for water in equilibrium with gasoline. However, as water moves through and away from the source area, relatively uncontaminated ground water will dilute the dissolved constituents to concentrations below gasoline/water equilibrium concentrations.

The high effective solubility of MtBE during dissolution from the gasoline phase means that MtBE will partition out of gasoline and into the aqueous phase more readily than will other fuel constituents (Squillace *et al.*, 1996, 1997, and 1998). The relatively lower effective solubilities of BTEX compounds indicates that a residual gasoline in soil can function as a continuing source, contributing BTEX contaminants to ground water for long periods of time. By contrast, because of its partitioning characteristics, MtBE in residual fuel sources is depleted more rapidly

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than other fuel constituents. Thus, the contribution of MtBE from a fuel spill to ground water may decrease markedly over time as the fuel becomes depleted in MtBE, while BTEX and other less mobile compound will remain in the source area.

Corseuil *et al.* (1998) found that ethanol concentrations greater than 10,000 µg/L will increase BTEX solubility and retard BTEX biodegradation. As a result, the addition of ethanol may result in migration of BTEX plumes farther from the source area (Kavanaugh and Stocking, 1999). Laboratory-observed and model-predicted impacts of ethanol on benzene include inhibited biodegradation and increased plume lengths, suggesting that the use of ethanol on remediation of fuel-impacted sites requires further evaluation (Deeb *et al.,* 2002).

A.4.2.2   Hydrodynamic Dispersion and Advection

Hydrodynamic dispersion is the process whereby a contaminant plume spreads and is the result of two processes: mechanical dispersion and diffusion (Weidemeier *et al.,* 1999). Because of hydrodynamic dispersion, the concentration of a solute will decrease with distance from the source.

Advective transport is the component of solute migration that is attributable to the movement of the water in which it is dissolved. In other words, after some period of time, a chemical dissolved in ground water will migrate a certain distance from the original source of the chemical as a consequence of the movement of water in the subsurface. In the absence of other effects (e.g., sorption, biodegradation), the migration velocity of the center of mass of a dissolved chemical slug is the average ground-water flow velocity.

As the dissolved chemical moves away from its source, it will mix with noncontaminated water resulting in a dilution of the contaminant by the process of *mechanical dispersion* (Fetter, 1999). Mechanical mixing occurs because each molecule of dissolved chemical follows a slightly different flowpath through the pore spaces within the porous medium; each also moves at a slightly different velocity. As ground water, containing dissolved chemical, moves along its tortuous flowpath in the subsurface, it tends to mix with water that contains no chemical (or contains the chemical at lower concentrations), diluting the dissolved-phase chemical.

Diffusion is the process by which both ionic and molecular species dissolved in water move from areas of higher concentration to areas of lower concentration. The net effect of diffusive processes acting on the dissolved contaminant as it migrates through a porous medium is that the mass of contaminant becomes distributed through an ever-increasing volume of subsurface material. This results in a decrease in concentration with increasing distance from the source. Diffusive processes do not actually remove chemical mass; therefore, decreases in chemical concentrations resulting from diffusion are associated with an increase in the volume of contaminated ground water.

Depending on local conditions, the primary mechanism by which dissolved constituents migrate in the saturated zone is usually advective transport, and the direction and rate of advective transport are controlled primarily by the hydraulic conductivity of the soil, and local hydraulic gradients (API, 1994; Reilly *et al.*, 1987; USEPA, 1989). However, it is possible for solutes to move through a porous medium by diffusion, even though the ground water is not flowing. Under conditions of very low or no ground-water flow, diffusion might cause a solute

to travel faster than the water is flowing. Under such conditions, diffusion is more important than advection in controlling contaminant migration (Gillham and Cherry, 1982; Fetter, 1999).

The dimensionless Peclet number ($\overline{P}$) can be used to identify the dominant ground-water transport process. The equation for calculating the Peclet number in the subsurface environment is:

$$\overline{P} \;=\; \frac{\overline{v} \times d_{characteristic}}{D_{liquid}^{water}} \tag{A-2}$$

where:

$\overline{v}$ = average solution velocity [L/T];

$d_{characteristic}$= some characteristic length of the porous medium (usually taken to be the mean grain diameter) [L]; and

D_{liquid}^{water} = chemical water-liquid diffusion coefficient [L^2/T].

The Peclet number provides a numerical measure of the relative importance of advection and diffusion in dispersing a dissolved constituent through a porous medium. At low ground-water flow velocities (less than approximately 30 feet per year) that result in low Peclet numbers, the dominant dispersion process is molecular diffusion. At higher velocities (high Peclet numbers), mechanical mixing processes and advection are more important. In general, contaminant transport in systems having Peclet numbers greater than about one (1.0), is dominated by advection with mechanical dispersion process. Conversely, contaminant transport in systems where the Peclet number is less than about 0.1 is dominated by diffusion (Gillham and Cherry, 1982).

A.4.2.3   Sorption

Sorption is the process of dissolved contaminants partitioning from the ground water to the aquifer mix. Sorption of dissolved contaminants results in slowing (retardation) of contaminant migration relative to the ground-water velocity and a reduction in dissolved contaminant concentrations in ground water. Sorption is a reversible reaction, and, as solute concentrations change, the relative amount of contaminants that are sorbing and desorbing will change. Sorption does not destroy solute mass; it merely retards migration. In most systems, chemical partitioning occurs at a rate that maintains chemical equilibrium (as expressed by the partition coefficient) between the sorbed and dissolved phases.

Sorption of dissolved contaminants is a complex phenomenon caused by several mechanisms, including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption (covalent bonding between chemical and aquifer matrix), dipole-dipole forces, dipole-induced dipole forces, and hydrophobic forces (Wiedemeier *et al.*, 1999). Because of their nonpolar molecular structure, hydrocarbons most commonly exhibit sorption through the process of hydrophobic bonding. When the particle surfaces of the aquifer matrix are less polar than the water molecule, as is generally the case, there is a strong tendency for the nonpolar contaminant molecules to partition from the ground water and sorb to the aquifer matrix. This

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phenomenon is referred to as hydrophobic bonding, and is an important factor controlling the fate of many organic pollutants in soils (Devinny *et al.*, 1990). Two components of an aquifer have the greatest effect on sorption: organic matter and clay minerals. In most aquifers, the organic fraction tends to control the sorption of fuel hydrocarbons.

Regardless of the sorption mechanism, it is possible to determine the amount of sorption to be expected when a given dissolved contaminant interacts with the materials comprising the aquifer matrix. Many bench-scale experiments have been performed by mixing water-contaminant solutions of various concentrations with aquifer materials containing various amounts of organic carbon and clay minerals. After equilibrium between the aqueous and sorbed phases has been reached, the amount of contaminant left in solution can be measured and expressed as a plot of the concentration of chemical sorbed versus the concentration remaining in solution. Because the experiments are performed at constant temperature, the relationship between the concentration of chemical sorbed and the concentration remaining in solution at equilibrium is referred to as the sorption isotherm.

The most commonly used method for expressing the distribution of an organic chemical between the aquifer matrix and the aqueous phase is the soil partition coefficient, or distribution coefficient, K_d, which is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration:

$$K_d = \frac{C_{sorbed}}{C_{dissolved}} \qquad\qquad (A-3)$$

where:

K_d = soil partition coefficient [L^3/M];

C_{sorbed} = concentration of chemical sorbed to soil [M/L^3]; and

$C_{dissolved}$ = concentration of chemical in adjacent soil water, at equilibrium with sorbed phase in soil [M/L^3].

Equation A-3 assumes that solid/liquid partitioning between the sorbed and dissolved phases is completely reversible, and that the equilibrium isotherm relating the relative concentrations in the two phases is linear (API, 1994; Lyman *et al.*, 1990). The linear isotherm is valid for a dissolved species that is present at a concentration less than one half of its solubility (Lyman *et al.*, 1992).

Soils are extremely heterogeneous mixtures of different particle types, composition, and sizes. Because of this heterogeneity, the partition coefficient for a particular chemical is usually regarded as a site-specific property and is likely to vary with location, chemical composition and soil grain-size distribution. However, sorption studies on a wide variety of nonpolar organic compounds and soil and sediment types indicate that organic matter in soil controls sorption where there is sufficient organic matter present (more than about 0.1 percent organic carbon). This observation has been used as the basis for normalizing the linear partition coefficient to the concentration of total organic carbon in the soil (Karickhoff *et al.*, 1979; Karickhoff, 1981). The normalized partition coefficient for a particular chemical (K_{oc}) is calculated from the results of sorption studies, using

$$C_s = K_d C \qquad\qquad (A\text{-}4)$$

where:

K_{oc} = organic carbon partition coefficient [L^3/M], and

f_{oc} = fraction of organic carbon in the soil [-].

If the organic carbon content of a particular soil is known or can be estimated, f_{oc} can be used, with published values of K_{oc} to estimate K_d using:

$$K_d = f_{oc} \times K_{oc} \qquad\qquad (A\text{-}5)$$

All hydrocarbon compounds, and most other chemicals, sorb to soil to a greater or lesser degree; the fraction of sorbed hydrocarbons increases as the concentration of organic carbon in the soil increases. Chemicals having larger values of partition coefficients will be more strongly adsorbed to soil and less mobile in the environment (Nyer and Skladany, 1989). This phenomenon is known as *retardation*; and the ratio of the velocity of the retarded chemical to local ground-water flow velocity is known as the *retardation coefficient* (*R*):

$$R = \frac{V_{ground\,water}}{V_{chemical}} = 1 + \left[\left(\frac{\rho}{n_e}\right) \times K_d\right] \qquad\qquad (A\text{-}6)$$

where:

$V_{ground\,water}$ = average ground-water flow velocity [L/T];

$V_{chemical}$ = average velocity of center of mass of dissolved chemical slug [L/T];

ρ = unit weight (bulk density) of porous medium [M/L^3]; and

n_e = effective porosity of the medium.

The degree of sorption and retardation are related to the partition coefficient of the compound and the organic carbon content of the aquifer. Because of its affinity for the aqueous phase (low distribution coefficient), retardation of MtBE is minimal in most ground-water systems. Under many circumstances, MtBE will move at a velocity very close to that of the advective ground-water flow velocity (Parsons, 1999). By contrast, BTEX will generally move in the aqueous phase at some fraction of the ground-water flow velocity. The differences in migration velocities between MtBE and BTEX constituents are most pronounced in porous media containing greater proportions of organic carbon. For example, if the organic carbon content of soil is 1 percent, MtBE will move at a velocity approximately one-half the advective ground water flow velocity, while BTEX constituents will migrate at velocities ranging from about one-tenth to one-twentieth the advective ground water flow velocity. The substantial differences in flow velocities among MtBE and BTEX compounds indicates that, if these substances are introduced to ground water at approximately the same time, the MtBE and BTEX plumes will separate with increasing migration distance from a fuel spill, as MtBE migrates more rapidly downgradient (Parsons, 1999).

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These predictions are verified by the results of large-scale surveys of MtBE behavior in the subsurface (e.g., Buscheck *et al.*, 1998; Happel *et al.,* 1998; Mace and Choi, 1998; Rong, 1999) and by individual case studies (Weaver *et al.*, 1996). In general, because MtBE is more mobile than the BTEX compounds, MtBE plumes can be more extensive than associated BTEX plumes, and may affect ground water at greater distances from gasoline spills than will BTEX. Furthermore, with increasing time in the subsurface, MtBE plumes and BTEX plumes have been observed to gradually disassociate, because of the disparity in migration velocities (Happel *et al.,* 1998). At a site on Long Island, New York, MtBE migrated a distance of nearly 6,000 feet from leaking gasoline USTs – more than 1,000 feet further than detectable concentrations of benzene. Although the benzene plume was nearly continuous from its source to maximum downgradient extent, the MtBE plume was observed to have detached from the contaminant source. MtBE had been rapidly depleted from the gasoline phase in the source area as a consequence of preferential partitioning from the fuel source to the aqueous phase.

A.4.3   Biodegradation Processes

Appendix B-5 of the original protocol (Air Force Center for Environmental Excellence [AFCEE], 1995) provides extensive discussion of the relationship between terminal electron accepting processes (TEAPs), electron acceptor/reaction endproduct formation, thermodynamics, local ground-water chemistry, and the ubiquity of suitable microorganisms for petroleum hydrocarbon biodegradation. The information provided in this addendum summarizes the key points from the original protocol. The goal of this section is to supplement information from the original protocol with recent advances in understanding of biodegradation processes at fuel-release sites.

A.4.3.1   Characteristics of Biodegradation at Fuel-Release Sites

More than three decades of research has produced numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of hydrocarbons, including components of gasoline, kerosene, diesel, and jet fuel (e.g., Jamison *et al.*, 1975; Atlas, 1981, 1984, and 1988; Young, 1984; Bartha, 1986; Wilson *et al.*, 1986 and 1990; Barker *et al.*, 1987; Baedecker *et al.*, 1988; Lee, 1988; Chiang *et al.*, 1989; Cozzarelli *et al.*, 1990; Leahy and Colewell, 1990; Alvarez and Vogel, 1991; Evans *et al.*, 1991a and 1991b; Edwards *et al.*, 1992; Edwards and Grbic-Galic, 1992; Thierrin *et al.*, 1992; Malone *et al.*, 1993; Davis *et al.*, 1994a and 1994b; Lovley *et al.*, 1995). In fact, almost all petroleum hydrocarbons are biodegradable. Under ideal conditions, the biodegradation rates of the low- to moderate-weight aliphatic, alicyclic, and aromatic compounds can be very high. As the molecular weight of the compound increases, so does the resistance to biodegradation (Atlas, 1988; Malone *et al.*, 1993).

Nearly all soils contain colonies of bacteria and fungi that are capable of biodegrading at least some organic compounds. **Table A.5** presents a partial list of the many microorganisms known to degrade petroleum hydrocarbons. Many genera of microorganisms are able to completely oxidize saturated, and to a lesser extent, aromatic hydrocarbons and heterocyclic compounds, to carbon dioxide (CO_2) and water. Although all organic compounds found in petroleum-based fuels can be degraded by bacteria (Dragun, 1988), the rates of fuel hydrocarbon degradation are slower under anaerobic conditions than are observed under aerobic conditions (Nyer and

TABLE A.5
SELECTED MICROORGANISMS DEMONSTRATED AS CAPABLE OF DEGRADING VARIOUS HYDROCARBONS

Contaminant	Microorganisms	Comments/ Biodegradability
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acinetobacter sp., Methylosinus trichosporium OB3b, Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium OB3b, Bacillus sp., Pseudomonas putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, Pseudomonas aeruginosa, Pseudomonas sp., Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High
MtBE	*Alcaligenes, Arthrobacter, Burkholderia, Gordonia, Graphium, Hydrogenophaga, Nocardia, Methylobacterium Mycobacterium Pseudomonas, Rodacoccus and Sphingomaonas*	Low to Moderate

Adapted from Riser-Roberts (1992) and Woodward and Sloan (2002).

Skladany, 1989). More recently, over 20 organisms with the capacity to biodegrade MtBE and other components of gasoline have been identified in surface soils, aquifers, wastewater treatment plants, and biofilters (Woodward and Sloan, 2002). Defined MtBE biodegradation pathways are predominantly aerobic, however recent evidence indicates that some organisms can utilize MtBE as a carbon and energy source by reducing iron in the presence of humates, or under methanogenic conditions (Finneran and Lovley, 2001). During biodegradation, microorganisms transform available nutrients (the "substrate") into forms useful for energy and cell reproduction by facilitating thermodynamically advantageous redox reactions involving the transfer of electrons from electron donors to electron acceptors. This results in oxidation of the electron donor and reduction of the electron acceptor. Electron donors can include natural organic material and anthropogenic hydrocarbon (e.g., BTEX) compounds. Electron acceptors are elements or compounds that occur in relatively oxidized states and can accept electrons generated during substrate oxidation. Without the complete transfer of electrons to an electron acceptor, a substrate cannot be fully oxidized. Electron acceptors commonly occurring in ground water include DO, nitrate, iron(III), manganese, sulfate, CO_2, and highly chlorinated solvents. In addition, manganese(IV) can act as an electron acceptor in some ground-water environments.

As described in AFCEE (1995) and Section 3.4.3.4.3, microorganisms preferentially utilize electron acceptors while metabolizing fuel hydrocarbons (Bouwer, 1992). Following release of fuels to the subsurface, dissolved oxygen (DO) is the first electron acceptor that is utilized in the biodegradation process. After DO is consumed, anaerobic microorganisms typically use native electron acceptors in the following order of preference: nitrate, manganese, ferric iron hydroxide, sulfate, and finally CO_2. In addition to being controlled by the energy yield of the reaction, the expected sequence of redox processes also is a function of the oxidizing potential of the ground water. This potential is a measure of the relative tendency of a solution or chemical reaction to

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accept or transfer electrons. As each subsequent electron acceptor is utilized, the ground water becomes more reducing, and the oxidation-reduction potential (ORP) of the water decreases. The main force driving this change in redox potential is microbially mediated redox reactions. ORP can be used as an indicator of which redox reactions may be operating at a site. Figure 3.3 illustrates the expected sequence of microbially mediated redox reaction. Local environmental conditions and microbial competition ultimately determine which TEAP will dominate a given location at a given time.

From a monitored natural attenuation (MNA) evaluation perspective, it is important to note that biodegradation causes measurable changes in ground-water geochemistry. During aerobic respiration, oxygen is reduced to water, and DO concentrations decrease. In anaerobic systems where nitrate is the electron acceptor, nitrate concentrations will decrease as this electron acceptor is reduced to nitrite, nitrous oxide, ammonia, or molecular nitrogen. In anaerobic systems where iron(III) is the TEAP, it is reduced to iron(II), and iron(II) concentrations increase. In anaerobic systems where sulfate is the TEAP, sulfate is reduced to hydrogen sulfide (H_2S), and sulfate concentrations decrease. In anaerobic systems where CO_2 is used as an electron acceptor, CO_2 is reduced by methanogenic bacteria, and methane is produced. During aerobic respiration, denitrification, iron(III) reduction, and sulfate reduction, total alkalinity will increase due to the biological production of CO_2. If methanogenesis is the dominant TEAP, alkalinity will remain fairly constant. **Table A.6** summarizes these trends. Changes in DO, nitrate, iron(II), sulfate, and methane concentrations can be used to ascertain the dominant TEAP. Lovley *et al.* (1994) suggest using dissolved hydrogen concentrations to determine the dominant TEAP. Although commercially available techniques for measurement of dissolved hydrogen are currently available, current practice suggests that wide-spread measurement of dissolved hydrogen concentrations in ground water at fuel-release sites does not add significant value to the quantification of biodegradation processes.

TABLE A.6
TRENDS IN CONTAMINANT, ELECTRON ACCEPTOR, METABOLIC BYPRODUCT, AND TOTAL ALKALINITY CONCENTRATIONS DURING BIODEGRADATION

Analyte	Terminal Electron Accepting Process	Trend in Analyte Concentration During Biodegradation
BTEX	---	Decreases
Dissolved Oxygen	Aerobic Respiration	Decreases
Nitrate	Denitrification	Decreases
Iron(II)	Iron (III) Reduction	Increases
Sulfate	Sulfate Reduction	Decreases
Methane	Methanogenesis	Increases
Alkalinity	Aerobic Respiration, Denitrification, Iron(III) Reduction, and Sulfate Reduction	Increases

Fuel hydrocarbons biodegrade naturally when an indigenous population of hydrocarbon-degrading microorganisms is present in the aquifer and sufficient concentrations of electron acceptors and nutrients are available to these organisms. In most subsurface environments, both aerobic and anaerobic degradation of fuel hydrocarbons will occur, often simultaneously in different parts of the plume. For thermodynamic reasons, microorganisms preferentially utilize those electron acceptors that provide the greatest amount of free energy during respiration (Bouwer, 1992). The rate of natural biodegradation generally is limited by a lack of electron

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acceptors rather than by a lack of nutrients such as ammonia, nitrate, or, phosphate. Studies at a jet-fuel-contaminated site noted little difference in biodegradation rates in areas with or without nutrient additions (Miller, 1990). These researchers concluded that nitrogen, phosphorus, and other trace nutrients were efficiently recycled by microorganisms at this site.

A.4.3.2   Stoichiometric Estimates of Biodegradation Effects

By using the half-cell reactions presented in Appendix B of AFCEE (1995), estimates for the mass of contaminant biodegraded per mass of electron acceptor consumed and/or the mass of reaction byproduct produced can be estimated. The purpose of developing these estimates is to supply input parameters for models of natural attenuation and/or to develop estimates for the assimilative capacity (either total or expressed), as described in Section 4 and in Wiedemeier *et al.* (1999).

As an example of the stoichiometric calculation procedure, consider the following equation that describes the complete mineralization of benzene (C_6H_6) to CO_2 under aerobic (i.e., oxygen-reducing) conditions in the absence of microbial cell production:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \qquad\qquad (A-7)$$

This stoichiometrically-balanced equation predicts that 7.5 moles of oxygen are required to reduce (or metabolize, in the case of a biologically mediated reaction) 1 mole of benzene. On a mass basis, the ratio of oxygen to benzene is given by:

Molecular weights: Benzene   6(12) + 6(1) = 78 gm/mol
                     Oxygen   7.5(32) = 240 gm/mol

Mass Ratio of Oxygen to Benzene = 240:78 = 3.08:1

Therefore, in the absence of microbial cell production, 3.08 mg of oxygen are required to completely metabolize 1 mg of benzene. Using the half-cell reactions for electron acceptors and BTEX compounds provided in Appendix B-5 of AFCEE (1995), similar calculations can be made for toluene, ethylbenzene, and xylene and used as input for analytical (e.g. BIOSCREEN) or numerical (e.g., BIOPLUME III) models that require input for an electron acceptor use coefficient. Stumm and Morgan (1995) provide a general equation that can be used to develop a half-cell reaction for complete mineralization of any hydrocarbon compound, given by:

$$\frac{1}{(4a+b)}C_aH_b + \frac{2a}{(4a+b)}H_2O \rightarrow \frac{a}{(4a+b)}CO_2 + H^+ + e^- \qquad (A-8)$$
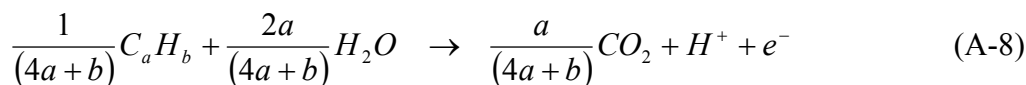
where the constants *a* and *b* represent the number of carbon and hydrogen atoms, respectively, in the original hydrocarbon compound. One example of how this half-cell reaction approach was applied to quantifying electron acceptor utilization of PAH compounds is presented in Brauner *et al.* (2002).

If the results of the conceptual site model (CSM) analysis suggest that a single or 'lumped' hydrocarbon substrate (e.g., total BTEX) modeling approach is appropriate, coefficients for each individual constituent of the 'lumped' hydrocarbon can be calculated, and a 'lumped' electron

acceptor utilization coefficient can be calculated for each TEAP by using a weighted-average approach. **Table A.7** summarizes the various ratios of total mass of BTEX degraded per mass of electron acceptor utilized or reaction byproduct produced for a 'lumped' hydrocarbon approach that assumes each individual BTEX constituent was found in equal molar proportion.

TABLE A.7
MASS RATIO OF ELECTRON ACCEPTORS REMOVED OR METABOLIC BY PRODUCTS PRODUCED TO TOTAL BTEX DEGRADED

Terminal Electron Accepting Process	Average Mass Ratio of Electron Acceptor to Total BTEX[a]	Average Mass Ratio of Metabolic Byproduct to Total BTEX [a]	Mass of BTEX Degraded per unit mass of Electron Acceptor Utilized (mg) [a]	Mass of BTEX Degraded per unit mass of Metabolic Byproduct Produced (mg) [a]
Aerobic Respiration	3.14:1	-----	0.32	-----
Denitrification	4.9:1	-----	0.21	-----
Iron(III) Reduction	41.9 [b]	21.8:1	0.02 [b]	0.05
Sulfate Reduction	4.7:1	-----	0.21	-----
Methanogenesis	-----	0.78:1	-----	1.28

[a] Simple average of all BTEX compounds based on individual compound stoichiometry.
[b] Assumes bioavailable iron(III) found as solid phase $Fe(OH)_3$.

The primary assumptions that underlie the stoichiometric calculations described in Equations (A-7) and (A-8) are that 1) the hydrocarbon substrate (e.g., BTEX) is completely degraded to CO_2 and 2) microorganisms do not use the hydrogen or carbon produced additional biomass. In reality, several intermediate products are produced from BTEX (or other hydrocarbon) biodegradation before total mineralization is achieved. This observation leads to the conclusion that the complete mineralization approach may underestimate the mass of hydrocarbon that could be degraded into an intermediate compound for a given mass of electron acceptor consumed. In addition, actual electron acceptor requirements may vary from those predicted by the stoichiometric relationships presented above because metabolic activity by the microbial population will use a portion of the biodegraded hydrocarbon for cell growth. Grady *et al.* (1999) demonstrated that stoichiometric formulations could be modified to account for microbial growth by 1) assuming that a portion of the growth substate (i.e., hydrocarbon) was converted into biomass and 2) accounting for this biomass production as a reaction endproduct using the empirical formula $C_5H_7O_2N$. Using this approach, and a bacterial yield coefficient (Y_m) that describes the amount of biomass produced per unit mass of substrate biodegraded (Grady *et al.*, 1999), Brauner *et al.* (2002) describe a process by which biomass production can be accounted for when using stoichiometric calculations for evaluating hydrocarbon degradation and associated electron acceptor utilization. Yields of microbial biomass vary depending on the thermodynamics of substrate biodegradation and on the availability of electron acceptor, nutrients, and substrate concentration (McCarty, 1971). Energy for cell maintenance is also needed, and this energy need is not reflected in the stoichiometric relationships presented above.

The culmination of these additional factors suggests that the electron acceptor demand predicted by stoichiometric calculations that do not account for partial hydrocarbon degradation and/or microbial growth will generally be higher than what would occur *in situ*. The implication of estimating use coefficients derived from 'pure' stoichiometry (i.e., no yield and complete mineralization) is that assimilative capacity and/or model calculations that are based on these calculations will predict that a larger mass of electron acceptor will be consumed during BTEX biodegradation than is actually occurring in the field (i.e., calculations will underestimate the amount of BTEX that can be biodegraded for a given mass of available electron acceptor). Conversely, the calculations presented above for BTEX compounds do not account for microbial consumption of the same electron acceptor mass that would be expected if biodegradation of other substrates (e.g., PAHs, naturally-occurring organic matter is also occurring). The implication of not accounting for non-BTEX compounds in stoichiometric equations is that the calculations will overestimate the amount of BTEX that can be biodegraded for a given mass of available electron acceptor. Although additional compounds could be included (either individually, or as additional 'lumped' substrates) in additional stoichiometric calculations, the most common approach to estimating use coefficients is to select values that are approximately equal to those calculated based on 'pure' stoichiometry. The basis for this practice is the assumption that the reduction in electron acceptor demand from partial degradation and microbial utilization on the same order of magnitude of excess electron acceptor demand that may be expressed from the presence of other substrates. In cases where BTEX is the primary substrate available for biological growth (e.g., total organic carbon concentrations in ground water are approximately equally to the total BTEX concentration), it may be justifiable to use a use coefficient that is up to 50 percent lower than would be predicted by 'pure' stoichiometry. The decision to adjust the use coefficient (up or down) in models that simulate natural attenuation will necessarily be a site-specific decision that should be based on a combination of available data, relative confidence in the accuracy and completeness of the CSM, and the complexity of the model being used to simulate the effects of natural attenuation.

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APPENDIX B

OVERVIEW OF STATE REGULATIONS AND GUIDANCE ON MONITORED NATURAL ATTENUATION OF FUEL-CONTAMINATED SITES

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B.0   INTRODUCTION

The following appendix was compiled to provide a snapshot in time (as of Spring 2003) of 1) how various states view the monitored natural attenuation (MNA) alternative and 2) which specific compounds are regulated in soil and ground water at fuel-release sites. The information provided in this appendix was based on available information collected from the various state agencies between Fall 2002 and Spring 2003, and is not intended to replace or otherwise alter compliance with current or future regulatory requirements or other guidance. For the most up-to-date information, it is recommended that users of this protocol review applicable state and/or federal regulations as these regulations change over time.

B.1   OVERVIEW OF STATE SURVEY APPROACH

The first data source used in compiling this summary of regulatory guidance on each state's position on MNA as a remedial option was a review of state regulatory websites. When available, MNA guidance documents were downloaded and reviewed for the information that was relevant to the evaluation and/or implementation of the MNA alternative. If a downloadable guidance document could not be easily located or obtained from the website, the state agency was contacted via phone or email with a request to provide more information on the existence or details of that state's MNA policy. Email and phone responses to these requests were documented, and referenced documents or hyperlinks (as provided by the agency) were reviewed.

During the review of available guidance documents, information relevant to evaluation and/or implementation of the MNA alternative was recorded. As summarized in **Table B.1**, the following information was compiled for each state: regulatory agency responsible for oversight of fuel-release site remediation, agency contact email address, agency website address, summary information on any existing state (fuel-specific) MNA guidance, and a listing of specific compounds that are regulated as part of the state underground storage tank (UST) program. Also summarized in Table B.1, is a review of available state guidance on MNA used to identify whether guidance was provided on the specific elements of a typical MNA investigation including site characterization, analytical protocol/requirements, data evaluation/analysis, site eligibility requirements, site closure requirements, site closure types, and long-term monitoring reporting/requirements.

B.2   SUMMARY OF STATE FUEL SITE ANALYTICAL REQUIREMENTS

Fuel-specific contaminants regulated by each state were obtained from the June 2002 issue of the Association for Environmental Health and Sciences' (AEHS) *Contaminated Soils, Sediments, and Water* (Nascarella *et al.*, 2002) and selected state guidance manuals. Required analyses for soil and ground water are summarized by state in the last two columns of Table B.1. **Figures B.1 through B.8** provide summary statistics on specific classes of contaminants that are regulated for soil and ground water in each state. Table B.1 and Figures B.1 through B.8 are provided at the end of this Appendix.

For purposes of summarizing state requirements for regulated fuel-related contaminants, the following discussion is divided into the following general classes of compounds: volatile organic

compounds (VOCs), semi-volatile organic compounds (SVOCs), total petroleum hydrocarbons (TPHs), and gasoline additives. While it is recognized that some gasoline additives (e.g., methyl tert-butyl ether [MtBE]) can also be categorized under one of the other existing categories (e.g., VOCs), gasoline additives are presented and discussed separately because the presence of these compounds at fuel-release sites is most commonly associated with releases from current or former gas station storage tanks.

B.2.1   Volatile Organic Compounds

The review of current regulatory requirements for soil quality characterization identified 39 states that specify standards for benzene, toluene, ethylbenzene and xylene isomer (BTEX) compounds as the sole requirement for VOC analysis of soils at fuel-release sites. Of the remaining states, 3 currently require VOC analysis in soil for benzene only, while 7 require analysis for a full suite of VOC concentrations in soil. Currently, one state (North Dakota) does not require any analysis for VOC concentrations in soil at fuel-release sites. Summary statistics of state requirements on VOC analysis for soil is provided as Figure B.1. Individual state requirements for VOC analysis in soils are listed in the second-to-last column of Table B.1.

For ground water, 43 states currently specify BTEX as the sole requirement for VOC analysis. Analysis for a complete range of VOCs in ground water is required by 4 states, whereas two states specify standards for benzene (only) in ground water. Currently, one state (Maryland) provides guidance, but has no promulgated standards, for VOCs (or any other chemical) in ground water. Summary statistics of state requirements on VOC analysis in ground water are provided as Figure B.2. Individual state requirements for analysis of VOCs in ground water are listed in the last column of Table B.1.

B.2.2   Semi-volatile Organic Compounds

SVOC analyses are commonly required at sites that are known or suspected to be contaminated with fuel (especially diesel) products. Two states (Connecticut and North Carolina) require a full analysis of SVOCs for both soil and ground water, while Indiana requires a full analysis of SVOCs only for ground water. Twenty-five states limit the required SVOC analysis to PAHs in both soil and ground water at fuel release sites. Of these 25 states, five states further limit the required SVOC analysis to naphthalene only if the fuel-release was gasoline. Six states specify naphthalene (only) analysis for soils, and seven states specify VOC analysis for naphthalene (only) in ground water. Figures B.3 and B.4 present summary statistics of state requirements on SVOC analysis in soils and ground water, respectively. As indicated on Figure B.3, current regulations in 17 states do not require SVOC analysis for soils at fuel-release sites. As indicated on Figure B.4, regulations in 15 states currently do not require SVOC analysis of ground water at fuel-release sites. Individual state requirements for SVOC analysis of soil and ground water are listed in the last two columns of Table B.1.

B.2.3   Total Petroleum Hydrocarbons

Currently, more than half of the state regulatory agencies are requiring analysis for entire classes of petroleum hydrocarbons in soil and/or groundwater. Although several states list TPH as a required analysis for fuel sites, the "TPH" designation does not, by itself, define a standard

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test. Rather, this term indicates the total concentration of hydrocarbons found within the boiling range specified as part of a particular analytical method and, in some cases, following extraction by a particular solvent (TPH Criteria Working Group, 1998). Although several states list TPH as a required analysis for fuel sites, further investigations (performed as part of this review) through correspondence with state agencies and an examination of required and preferred laboratory analytical methods indicate that the "TPH" analysis requirement most commonly refers to the petroleum hydrocarbon range for gasoline-range organics (GRO) and/or diesel-range organics (DRO), depending on the type of fuel released. GRO, which corresponds to the C_6 to C_{10} range of alkanes, and DRO, which corresponds to the C_{10} to C_{28} range of alkanes, are measured using United States Environmental Protection Agency (USEPA) Method SW8015B. Based on the current review of state regulations, GRO/DRO analyses were identified as the preferred TPH measurements for soil and ground water in 30 and 22 states, respectively.

Other states that require TPH analysis often use a state-specific analytical method rather than a standard USEPA method. For example, some states have developed state-specific analytical methods that provide definitions and method descriptions for new "classes" of TPH including volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH). Measurements of VPH and/or EPH are now used by four states requiring TPH for soil and groundwater. In addition, two other states (Iowa and Connecticut) have developed state-specific methods for total extractable hydrocarbons (TEH), and have subsequently used these methods to quantify TPH concentrations in both soil and ground water. One state (Alabama) specifies various USEPA methods that can be used for analysis of TPH in soil. Finally, two states (Florida and Nebraska) have developed state-specific methods to analyze for TRPH, as the previous standard method for TRPH measurement (USEPA Method 418.1) has been deleted in response to a federally-mandated ban on "non-essential" use of the Freon solvent specified in this method.

Summary statistics of state requirements on TPH analysis in soil and ground water are provided as Figure B.5 and Figure B.6, respectively. Individual state requirements for TPH requirements are listed in the last two columns of Table B.1. Given the variation in requirements and methods for assessing TPH at fuel-release sites, users of this protocol addendum are encouraged to review state- and site-specific requirements prior to obtaining TPH data, with the objective of ensuring that the type of sample collection and analysis performed is consistent with the requirements of the regulatory agencies charged with oversight of site remediation and closure.

B.2.4   Gasoline Additives

Analytical requirements and standards for fuel oxygenates vary greatly by state. Analysis for MtBE in soil and ground water is required in 20 states and 26 states, respectively (Figures B.7 and B.8). Nine states require analysis for lead in soil, and 11 require lead analysis for ground water. Analysis for the additives EDC (ethylene dichloride or 1,2-dichloroethane) and EDB (ethylene dibromide or 1,2-dibromomethane), which were commonly used to solubilize lead in leaded gasoline, is required by three states for soil and five states for ground water. One state (Kansas) requires only EDC analysis for both soil and ground water, and another state (Nebraska) limits analytical requirements for potential gasoline additives to EDB and MTBE. California specifies a broad category of analyses for "oxygenates". A review of California UST

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guidance indicates this category of chemicals includes all oxygenates that can be detected using USEPA Method 8260B, resulting in an "expanded" analyte reporting list for VOCs.

B.3   COMMON ELEMENTS OF STATE MNA GUIDANCE

MNA information was obtained from 48 states. The two states with missing data (Nebraska and Rhode Island) did not respond to requests for further information on their MNA policy. Of the states that provided information, 47 allow MNA as a remedy for fuel-contaminated ground water. Two of these states indicated specifically that MNA is allowed on a site-by-site basis, and one state requires that MNA be performed in conjunction with some other ongoing remediation activity. A total of 17 states have MNA guidance that is either specifically written for fuel-release sites or references petroleum hydrocarbons as COCs that qualify for remediation by MNA. Several states reported that they have no existing MNA guidance; however these states allow MNA as a remedy for petroleum hydrocarbon contamination. In most cases, these states refer to USEPA, American Society for Testing and Materials (ASTM), or Interstate Technology Regulatory Council (ITRC) guidance when MNA is considered to be a viable remedial option at a particular site.

The level of detail included in state MNA guidance documents varied widely from state to state. Most of the available documents outline requirements for site characterization, analytical protocol, data evaluation/analysis, long-term monitoring (LTM), and the eligibility of the site for the use of MNA. Fewer documents addressed the requirements for free product recovery and site closure.

B.4   REFERENCES

Nascarella, M.A., Kostecki, P., Calabrese, E., and Click D. 2002. 2001 Survey of states' soil and groundwater cleanup standards. *Contaminated Soil, Sediment & Water*. Associated Environmental Health and Sciences (AEHS). January/February.

TPH Criteria Working Group. 1998. *Volume 1: Analysis of Petroleum Hydrocarbons in Environmental Media* (W. Weisman, Ed.). Amherst Scientific Publishers, Amherst, MA. March. 98pp. (Available in electronic format from www.aehs.com)

State-Specific MNA Guidance

	State Regulatory Agency, Responsible Division, and Contact Information for Remediation of Fuel-Release Sites	Available MNA Site Remediation Guidance — Fuel Sites?	Other Sites?	If guidance is available, what state program administers regulations?	If no Guidance exists at all, any under development?	Is MNA an allowable fuel remedy?	Site Characterization?	Analytical Protocol/ Requirements?	Data Evaluation/ Analysis?	Eligibility Requirements?	Free Product Recovery Requirements?	Site Closure Requirments?	Site Closure Types?	Long-Term Monitoring/ Reporting Requirements?	Fuel-Specific Contaminants Regulated by UST Program[a/] — Soil	Groundwater
USEPA	*Agency:* Office of Solid Waste and Emergency Response *Contact:* *Email:* *Website:* http://www.epa.gov/swerust1/oswermna/index.htm	Yes	Yes; chlorinated solvents	N/A	N/A	Yes	Yes	No	No	Yes	Yes	No	N/A	Yes	N/A	N/A
Alabama	*Agency:* DEM, Land Division *Contact:* No contact specified *Email:* Landmail@adem.state.al.us *Website:* http://www.adem.state.al.us/LandDivision/LandDivisionPP.htm	No	Yes (generic - but mentions petroleum in text)	Hazardous Waste Program	N/A	Yes	No	No	No	No	No	No	Not included	No	BTEX, TPH[b/], MTBE, PAHs	BTEX, MTBE, PAHs
Alaska	*Agency:* DEC, Division of Spill Prevention and Response *Contact:* No contact specified *Email:* website@envircon.state.ak.us *Website:* http://www.state.ak.us/local/akpages/ENV.CONSERV/home.htm	No	Yes (generic - but mentions petroleum in text)	Contaminated Sites Remediation Program	No	Yes	Yes	No	No	Yes	No	No	Not included	Yes	BTEX, GRO/DRO, naphthalene, PAHs	BTEX, GRO/DRO, naphthalene, PAHs
Arizona	*Agency:* DEQ, Waste Programs Division, Rules and Risk Assessment *Contact:* Ren Willis-Frances *Email:* willis-frances.ren @ev.state.az.us *Website:* http://www.adeq.state.az.us/environ/waste/capdev/risk.html	Yes	Yes (generic)	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	No	Yes	Not included (may be in accompanying document)	No (may be in accompanying document)	BTEX, MTBE, GRO/DRO, PAHs	BTEX, TPH, MTBE, Benzopyrene
Arkansas	*Agency:* DEQ, RST Program *Contact:* James Atchley *Email:* atchley@adeq.state.ar.us *Website:* http://www.adeq.state.az.us/environ/waste/capdev/risk.html	No	No	UST Program	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, PAHs	BTEX, MTBE, PAHs
California	*Agency:* EPA, Department of Toxic Subtances Control *Contact:* Noel Laverty *Email:* nlaverty@dtsc.ca.gov *Website:* http://www.dtsc.ca.gov/index.html	No	No	N/A	No; defer to USEPA	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH[c/], TRPH, HVOs, Oxygenates	BTEX, TPH[c/], TRPH, HVOs, Oxygenates
Colorado	*Agency:* Colorado Division of Labor and Employment, Division of Oil and Public Safety *Contact:* No contact specified *Email:* oil.publicsafety@state,co,us *Website:* http://oil.cdle.state.co.us/OIL/Technical/oistech.asp	Yes	No	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	No	Yes	NFA	Yes	BTEX, TPH, naphthalene	BTEX, TPH, naphthalene
Connecticut	*Agency:* DEP, Bureau of Water Management *Contact:* Christine Lacas *Email:* christine.lacas@po.state.ct.us *Website:* http://dep.state.ct.us/index.htm	No	No	N/A	No; defer to USEPA	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Call DEP UST Division	Call DEP UST Division
Delaware	*Agency:* DNREC, Site Investigation and Restoration/Brownfields Branch *Contact:* Rittberg Alex *Email:* Alex.Rittberg@state.de.us *Website:* http://www.dnrec.state.de.us/dnrec2000/	No	No	N/A	No; defer to USEPA and ITRC guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, lead, EDB/EDC, GRO/DRO	BTEX, MTBE, lead, EDB/EDC, Cumene, naphthalene
Florida	*Agency:* DEP, Division of Waste Mgt., Bureau of Petroleum Storage Systems *Contact:* Roger Rook *Email:* Roger.Rook@dep.state.fl.us *Website:* http://www.dep.state.fl.us/	Yes	No	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	NFA	Yes	BTEX, MTBE, PAHs, metals, TRPH[d/]	BTEX, MTBE, PAHs, EDB/EDC, metals, TRPH[d/]
Georgia	*Agency:* EPD, UST Management Program and Haz Waste Corrective Action Program *Contact:* Ted Jackson *Email:* Ted_Jackson@dnr.state.ga.us *Website:* http://www.dnr.state.ga.us/environ/	Yes	No	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	NFAR	Yes	BTEX, PAHs, GRO/DRO	BTEX
Hawaii	*Agency:* DOH, Environmental Management Division *Contact:* Patrick Felling *Email:* pfelling@eha.health.state.hi.us *Website:* http://www.state.hi.us/health/eh/	Yes	No	Hazardous Waste Program	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	NFAR	Yes	BTEX, MTBE, GRO/DRO, naphthalene	BTEX, MTBE, GRO/DRO, PAHs
Idaho	*Agency:* DEQ, *Contact:* Joseph Nagel *Email:* jnagel@deq.state.id.us *Website:* http://www.deq.state.id.us/waste/waste1.htm	Yes	Yes	RBCA	N/A	Yes	Yes	No	Yes	Yes	Yes	No	Not Included	Yes	BTEX, MTBE, PAHs	BTEX, MTBE, PAHs
Illinois	*Agency:* EPA *Contact:* Greg Dunn *Email:* Greg.Dunn@epa.state.il.us *Website:* http://www.epa.state.il.us/land/cleanup-programs/	No	No	N/A	No	Typically no, exceptions may be granted	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, PAHs	BTEX, PAHs

State-Specific MNA Guidance

State	State Regulatory Agency, Responsible Division, and Contact Information for Remediation of Fuel-Release Sites	Fuel Sites?	Other Sites?	If guidance is available, what state program administers regulations?	If no Guidance exists at all, any under development?	Is MNA an allowable fuel remedy?	Site Characterization?	Analytical Protocol/ Requirements?	Data Evaluation/ Analysis?	Eligibility Requirements?	Free Product Recovery Requirements?	Site Closure Requirments?	Site Closure Types?	Long-Term Monitoring/ Reporting Requirements?	Soil	Groundwater
Indiana	Agency: DEM, Office of Land Quality, LUST Program Contact: Jeff Turley Email: jturley@dem.state.in.us Website: http://www.in.gov/idem/land/lust/	Yes	No	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	No	No	N/A	Yes	GRO/DRO	BTEX, MTBE, SVOCs
Iowa	Agency: DNR, UST Program Contact: Jim Humeston Email: jim.humeston@dnr.state.ia.us Website: http://www.state.ia.us/dnr/organiza/wmad/lqbureau/ust/index.html	No	No	N/A	No	Yes; low risk sites monitor COCs	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TEH[e/]	BTEX, TEH[e/]
Kansas	Agency: DHE Contact: Rick Bean Email: rbean@kdhe.state.ks.us Website: http://www.kdhe.state.ks.us/remedial/index.html	No	Yes (generic)	General Remedial Program	N/A	Yes	Yes	Yes	No	Yes	Yes	No	Not included	Yes	benzene, GRO/DRO, EDC	BTEX, EDC, naphthalene
Kentucky	Agency: Natural Resources and Environmental Protection Cabinet Contact: Matthew Hackathorn Email: Matthew.Hackathorn@mail.state.ky.us (webmaster) Website: http://www.nr.state.ky.us/nrepc/programs.htm	No	No	N/A	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, PAHs, lead	BTEX, PAHs, lead
Louisiana	Agency: DEQ, Toxicological Services Section Contact: Tom Harris Email: tharris@deq.state.la.us Website: http://www.deq.state.la.us/	Yes	Yes	Risk Evaluation/ Corrective Action Program	N/A	Yes	Yes	Yes	Yes	Yes	Yes	No	Not included	Yes	TPH[e/], SVOCs, metals, benzene	TPH[e/], SVOCs, metals, benzene
Maine	Agency: DEP, Division of Remediation Contact: Ted Wolfe Email: theodore.e.wolfe@state.me.us Website: http://www.state.me.us/dep/	No	No	N/A	No	Yes; case-by-case basis	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	GRO/DRO	benzene, MTBE, GRO/DRO
Maryland	Agency: MDE Contact: Art O'Connell Email: Website: http://www.mde.state.md.us/index.asp	No	No	N/A	No; defer to USEPA guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, GRO/DRO, naphthalene	Call MDE - no promulgated standards
Massachusetts	Agency: DEP, Bureau of Waste Site Cleanup Contact: John Fitzgerald Email: John.J.Fitzgerald@state.ma.us Website: http://www.state.ma.us/dep/dephome.htm	No	No	No	No; defer to USEPA, ASTM, ITRC, NAS G125guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, PAHs, VPH/EPH[e/]	BTEX, MTBE, PAHs, VPH/EPH[e/]
Michigan	Agency: DEQ, Remediation & Development Division Contact: Carl Chavez Email: chavezc@michigan.gov Website: http://www.michigan.gov/deq	No	No	N/A	No; defer to USEPA, ASTM and/or AFCEE guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, lead, PAHs	BTEX, MTBE, lead, PAHs
Minnesota	Agency: PCA, Site Remediation Section Contact: Email: http://www.pca.state.mn.us/ask.html Website: http://www.pca.state.mn.us/netscape4.html	Yes	Yes; chlorinated organics	Groundwater & UST Programs	N/A	Yes	No	Yes	Yes	No	No	No	Not included	No	TPH[c/], VOCs, MTBE	TPH[c/], VOCs
Mississippi	Agency: DEQ, UST Branch Contact: Martha Martin Email: martha_martin@deq.state.ms.us Website: http://www.deq.state.ms.us/newweb/homepages.nsf	No	No	N/A	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, PAHs	BTEX, PAHs
Missouri	Agency: DNR, Hazardous Waste Program Contact: Outreach Center Email: oac@mail.dnr.state.mo.us Website: http://www.dnr.state.mo.us/dsp/homedsp.htm	Yes	Yes	Voluntary Cleanup Program	N/A	Yes	Yes	No	Yes	Yes	No	Yes	unrestricted and restricted	No	BTEX, MTBE, GRO/DRO	BTEX, MTBE, GRO/DRO, PAHs
Montana	Agency: DEQ, Hazardous Waste Site Cleanup Bureau Contact: Michael Trombetta Email: mtrombetta@state.mt.us Website: http://www.deq.state.mt.us/	No	No	N/A	No; defer to USEPA guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, VPH/EPH[e/], PAHs	BTEX, MTBE, VPH/EPH[e/], PAHs
Nebraska	Agency: DEQ Contact: Email: MoreInfo@NDEQ.state.NE.US Website: http://www.deq.state.ne.us	No documentation provided on state website or in response to request for further information.													BTEX, TRPH[d/], VOCs, SVOCs	BTEX, TRPH[d/]
Nevada	Agency: Division of Environmental Protection Contact: Jennifer Carr Email: jcarr@ndep.state.nv.us Website: http://ndep.nv.gov/	No	No	N/A	No; defer to USEPA guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	GRO/DRO	BTEX

State-Specific MNA Guidance

State	State Regulatory Agency, Responsible Division, and Contact Information for Remediation of Fuel-Release Sites	Available MNA Site Remediation Guidance — Fuel Sites?	Other Sites?	If guidance is available, what state program administers regulations?	If no Guidance exists at all, any under development?	Is MNA an allowable fuel remedy?	Site Characterization?	Analytical Protocol/ Requirements?	Data Evaluation/ Analysis?	Eligibility Requirements?	Free Product Recovery Requirements?	Site Closure Requirments?	Site Closure Types?	Long-Term Monitoring/ Reporting Requirements?	Fuel-Specific Contaminants Regulated by UST Program[a] — Soil	Groundwater
New Hampshire	Agency: DES, Waste Management Division Contact: Email: remed@des.state.nh.us hwcomp@des.state.nh.us Website: http://www.des.nh.us/orcb_hwrb.htm	No	Yes (VOCs)	Hazardous Waste Program	N/A	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	VOCs, GRO/DRO, PAHs	BTEX, MTBE, benzo(a)pyrene, naphthalene
New Jersey	Agency: DEP Contact: Maria Franco-Spera Email: Website: http://www.nj.gov/dep/	No	No	N/A	No	Yes	No information could be obtained								BTEX, PAHs, lead	BTEX, MTBE, TBA, naphthalene, lead
New Mexico	Agency: Environment Department Ground Water Quality Bureau Contact: Dennis McQuillan Email: dennis_mcquillan@nmenv.state.nm.us Website: http://www.nmenv.state.nm.us/	No	Yes	Groundwater Quality	Yes (draft guidance exists for petroleum and non-petroleum); also defer to ASTM	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, GRO/DRO, EDB/EDC, PAHs, lead	BTEX, MTBE, GRO/DRO, EDB/EDC, PAHs, lead
New York	Agency: DEC Contact: Jim Harrington Email: jbharrin@gw.dec.state.ny.us Website: http://www.dec.state.ny.us/	No	No	N/A	No; defer to USEPA	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, PAHs	BTEX, MTBE, PAHs
North Carolina	Agency: DENR, Division of Waste Management Contact: Chrystal Bartlett Email: chrystal.bartlett@ncmail.net Website: http://ust.ehnr.state.nc.us/	No	Yes; chlorinated organics	Hazardous Waste Program	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	TPH[e], VOCs, SVOCs, metals	TPH[e], VOCs, SVOCs, metals
North Dakota	Agency: DOH Environmental Health Division Contact: Gary Berreth Email: gaberreth@state.nd.us Website: http://www.health.state.nd.us/ndhd/environ/	No	No	N/A	No	Yes; case-by-case basis	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, GRO/DRO	BTEX, GRO/DRO
Ohio	Agency: EPA, Division of Hazardous Waste Management Contact: Pam Allen Email: pam.allen@epa.state.oh.us Website: http://www.epa.state.oh.us/dhwm/welcome.html	No	No	Hazardous Waste Program	No; defer to USEPA	Yes; in conjunction with ongoing active remediation	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, GRO/DRO, PAHs	BTEX, GRO/DRO, PAHs
Oklahoma	Agency: DEQ, Land Protection Division Contact: Catherine Sharp Email: Catherine.Sharp@deq.state.ok.us Website: http://www.deq.state.ok.us/LPDnew/index.htm	No	Yes (generic)	Land Protection	N/A	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH	BTEX, TPH
Oregon	Agency: DEQ, Land Quality Division Contact: Michael Anderson Email: anderson.michael@deq.state.or.us Website: http://www.deq.state.or.us/	No	No	N/A	No; defer to USEPA guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH[c], PAHs, lead, EDB/EDC	BTEX, MTBE, PAHs, EDB/EDC
Pennsylvania	Agency: DEP, Division of Remediation Services Contact: Arnold Micheal Email: miarnold@state.pa.us Website: http://www.dep.state.pa.us/	No	No	No	No; defer to ITRC guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, PAHs, lead	BTEX, MTBE, PAHs, EDB/EDC, lead
Rhode Island	Agency: DEM, Contact: Michael Cote Email: mcote@dem.state.ri.us Website: http://www.state.ri.us/dem/	No documentation provided on state website or in response to request for further information.														BTEX, MTBE, GRO/DRO, naphthalene	BTEX, MTBE, naphthalene
South Carolina	Agency: DHEC, UST Program Contact: Art Shrader Email: shradeaa@columb26.dhec.state.sc.us Website: http://www.scdhec.net/	Yes	Yes	UST Program	N/A	Yes	Yes	Yes	Yes	Yes	No	Yes	NFA, CNFA	Yes	BTEX, MTBE, EDB, PAHs	BTEX, MTBE, EDB, PAHs
South Dakota	Agency: DENR, Ground Water Quality Program Contact: Bill Markley Email: Bill.Markley@state.sd.us Website: http://www.state.sd.us/denr/DES/Ground/groundprg.htm	Yes	No	Ground Water Quality Program	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	NFA	Yes	BTEX, TPH[c], naphthalene	BTEX, TPH[c]

State-Specific MNA Guidance

| State	State Regulatory Agency, Responsible Division, and Contact Information for Remediation of Fuel-Release Sites	Available MNA Site Remediation Guidance — Fuel Sites?	Available MNA Site Remediation Guidance — Other Sites?	If guidance is available, what state program administers regulations?	If no Guidance exists at all, any under development?	Is MNA an allowable fuel remedy?	Site Characterization?	Analytical Protocol/ Requirements?	Data Evaluation/ Analysis?	Eligibility Requirements?	Free Product Recovery Requirements?	Site Closure Requirments?	Site Closure Types?	Long-Term Monitoring/ Reporting Requirements?	Fuel-Specific Contaminants Regulated by UST Program[a] — Soil	Fuel-Specific Contaminants Regulated by UST Program[a] — Groundwater
Tennessee	Agency: DEC, UST Program; Contact: Clayton Bullington RCRA Program; Email:; Website: http://www.state.tn.us/environment/ust/index.html	No	No	N/A	No; defer to USEPA Region IV guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	TPH[b], benzene	TPH[b], benzene
Texas	Agency: Texas Commission on Environmental Quality/Texas Natural Resources Conservation Commission, Remediation Division; Contact:; Email: http://www.tnrcc.state.tx.us/homepgs/oprr.html; Website: http://163.234.20.106/index.html	No	Yes (generic)	Texas Risk Reduction Program (TRRP)	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH[b], PAHs	BTEX, TPH[b], PAHs
Utah	Agency: DEQ, Department of Environmental Response and Remediation; Contact:; Email: deqinfo@deq.state.ut.us; Website: http://www.eq.state.ut.us/	No	No	N/A	No; defer to USEPA guidance	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, GRO/DRO, naphthalene	BTEX, MTBE, GRO/DRO, naphthalene
Vermont	Agency: DEC, Waste Management Division; Contact: Skip Flanders; Email: skipf@dec.anr.state.vt.us; Website: http://www.anr.state.vt.us/dec/dec.htm	No	Yes (generic)	No	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH[b]	BTEX, MTBE
Virginia	Agency: DEQ, UST Branch; Contact: Fred Cunningham; Email: fkcunningham@deq.state.va.us or James Barnett; Website: http://www.deq.state.va.us	No	No	N/A	No	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, GRO/DRO	BTEX, GRO/DRO
Washington	Agency: Department of Ecology; Contact: Hun S. Park; Email: HPar461@ecy.wa.gov; Website: http://www.ecy.wa.gov/	No	No	N/A	Yes	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, TPH[c]	BTEX, TPH[c]
West Virginia	Agency: DEP, Office of Environmental Remediation; Contact:; Email: jgreathouse@dep.state.wv.us; Website: http://www.dep.state.wv.us/	Yes	Yes (generic)	Voluntary Cleanup Program	N/A	Yes	Yes	No	No	No	Yes	N/A	Not included	N/A	BTEX, GRO/DRO	BTEX, GRO/DRO
Wisconsin	Agency: DNR, Bureau for Remediation and Redevelopment; Contact: Mark F. Giesfeldt; Email: Mark.Giesfeldt@dnr.state.wi.us; Website: http://www.dnr.state.wi.us/	Yes	No	Remediation and Redevelopment Program	N/A	Yes	Yes	Yes	Yes	Yes	No	Yes	Not included	Yes	BTEX, MTBE, VOCs, PVOCs, TPH[c], PAHs, TMB	BTEX, MTBE, VOCs, PVOCs, TPH[c], PAHs, TMB
Wyoming	Agency: DEQ, Solid and Hazardous Waste; Contact: Carl Anderson; Email: CANDER@state.wy.us; Website: http://deq.state.wy.us/	No	No	Voluntary Cleanup Program	Yes	Yes	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	BTEX, MTBE, total lead, GRO/DRO, naphthalene	BTEX, MTBE, total lead, GRO/DRO, naphthalene

BTEX = benzene, toluene, ethylbenzene, xylene
DRO = diesel range organics
EDB = 1,2 dibromoethane
EDC = 1,2 dichlorethane
EPH = extractable petroleum hydrocarbons
GRO = gasoline range organics
HVO = halogenated volatile organics
MTBE = methyl-tert-butyl ether
PAH = polycyclic aromatic hydrocarbon
PCB = polychlorinated biphenyl
PVOC = petroleum volatile organic compounds
SVOC = semi-volatile organic compounds
TCLP = Toxic Characteristic Leaching Procedure
THE = total extractable hydrocarbons
TOX = total organic halogens
TPH = total petroleum hydrocarbon
TRPH = total recoverable petroleum hydrocarbon
VOC = volatile organic compounds
VPH = volatile petroleum hydrocarbons

DEC = Department of Environmental Conservation
DEM = Department of Environmental Management
DENR = Department of Environment and Natural Resources
DEP = Department of Environmental Protection
DEQ = Department of Environmental Quality
DES = Department of Environmental Services
DHE = Department of Health and Environment
DNR = Department of Natural Resources
DNREC = Department of Natural Resources and Environmental Conservation
DOH = Department of Health
EPD = Environmental Protection Division
MDE = Maryland Department of the Environment
PCA = Pollution Control Agency

N/A = not applicable
NFA = no further action
NFAR = no further action required
RBCA = risk-based corrective action
RST = registered storage tank
USEPA = United States Environmental Protection Agency
UST = underground storage tank

[a] Source: AEHS, 2002.
[b] State-specific method is used to determine TPH.
[c] State-specific method is used to determine TPH as GRO/DRO.
[d] State-specific method is used to determine TRPH.
[e] State-specific method is used to determine TPH as VPH/EPH or TEH.

Figure B.1
Summary of State Regulatory Requirements for VOCs
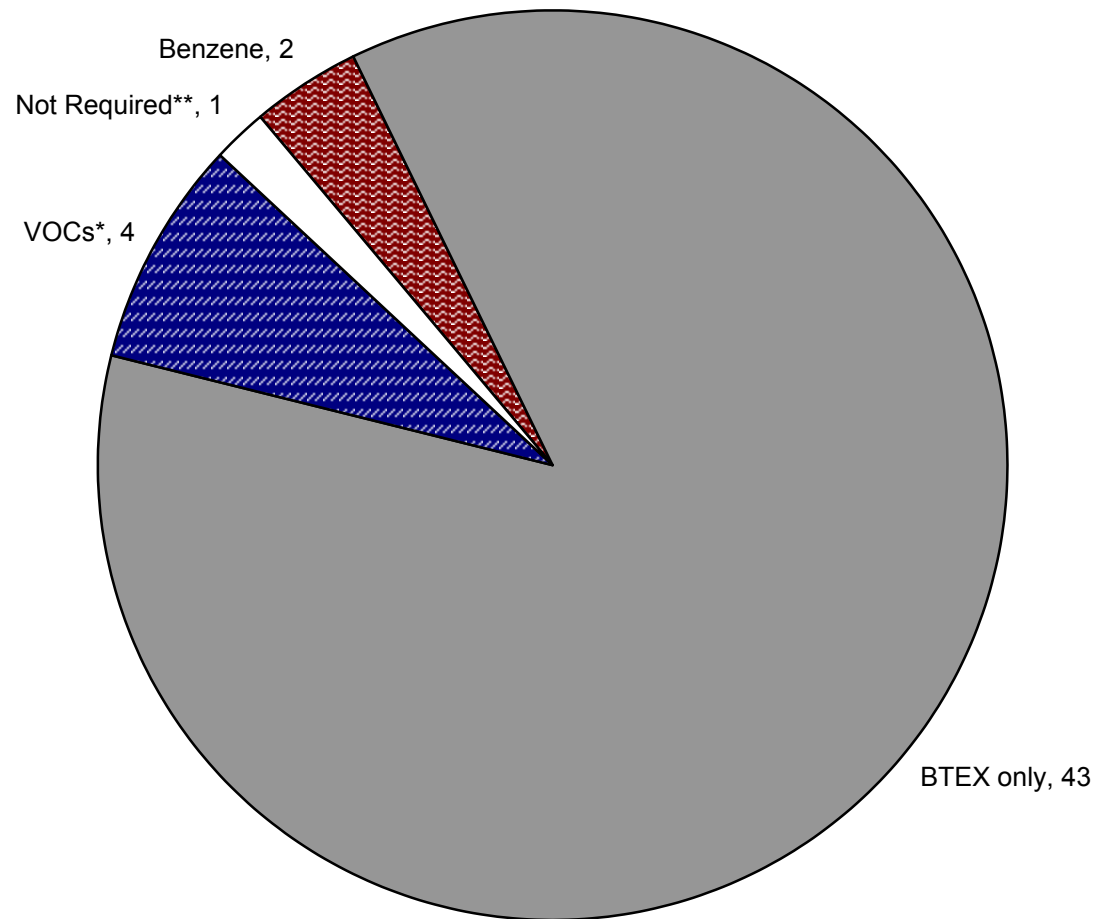**in Soil at Fuel-release Sites**

Not Required**, 1

Benzene only, 3

VOCs*, 7

BTEX only, 39
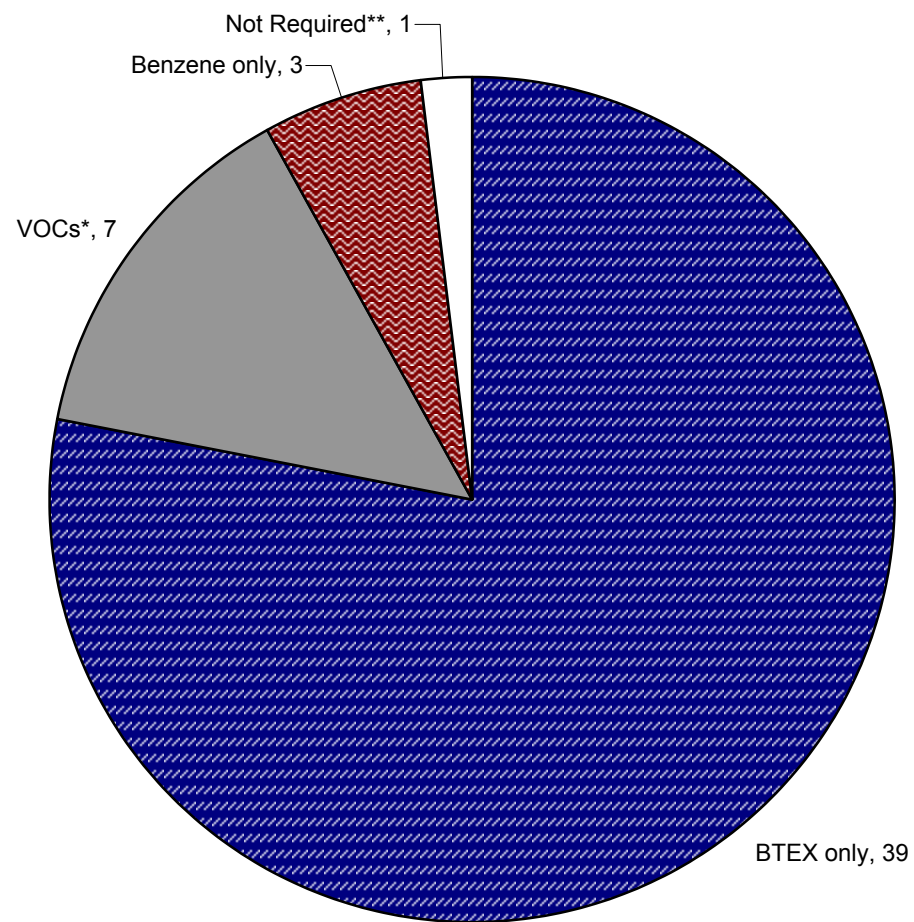
*Wisconsin specifically requires BTEX and trimethylbenzenes as part of the VOC analysis.
**North Dakota requires BTEX analysis for groundwater only.
Note: BTEX = benzene, toluene, ethylbenzene, and xylene isomers; VOC = volatile organic compound

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Figure B.2
Summary of State Regulatory Requirements for VOCs
in Ground Water at Fuel-release Sites

*Wisconsin specifically requires BTEX and trimethylbenzenes as part of the VOC analysis.
**There are no promulgated cleanup standards for ground water in Maryland.
Note: BTEX = benzene, toluene, ethylbenzene, and xylene isomers; VOC = volatile organic compound

Figure B.3
Summary of State Regulatory Requirements for SVOCs
in Soil at Fuel-release Sites
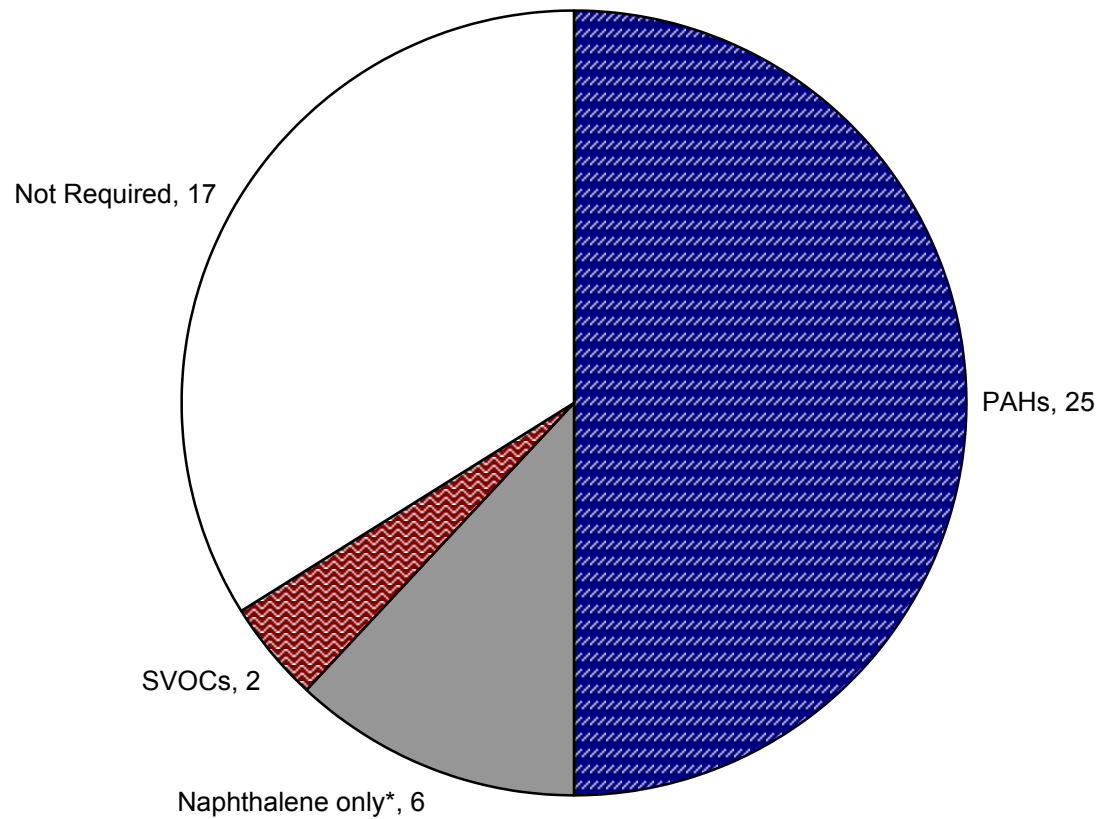
Not Required, 17

PAHs, 25

SVOCs, 2

Naphthalene only*, 6

**Colorado may require analyses for additional priority PAHs at sites where TPH concentrations are above 500 milligrams per kilogram.
Note: SVOC = semi-volatile organic compound; PAH = polycyclic aromatic hydrocarbon; TPH = total petroleum hydrocarbon

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Figure B.4
Summary of State Regulatory Requirements for SVOCs
in Ground Water at Fuel-release Sites
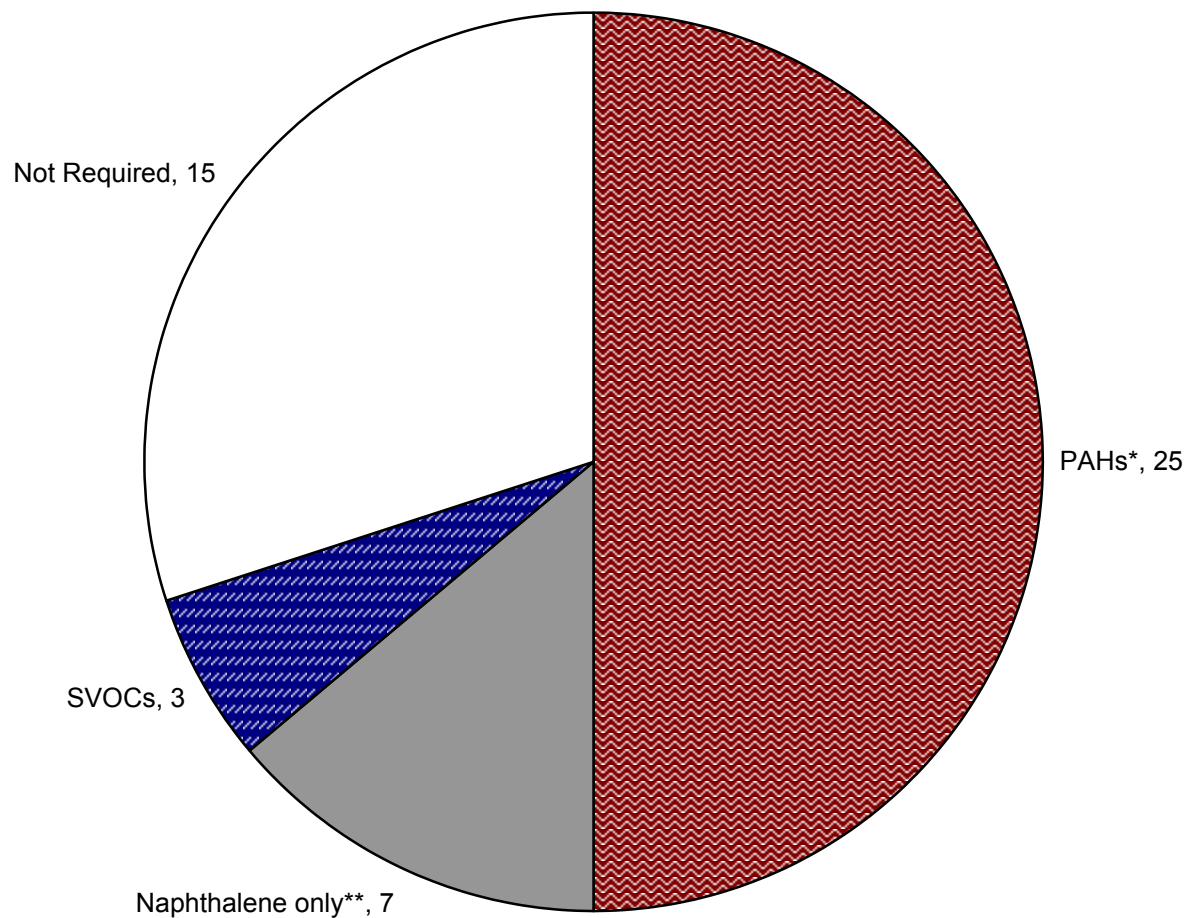
*South Carolina requires naphthalene and total PAH analyses. Five states require only naphthalene at gasoline-contaminated sites.
**Colorado may require analyses for additional priority PAHs at sites where TPH concentrations are above 500 milligrams per kilogram.
Note: SVOC = semi-volatile organic compound; PAH = polycyclic aromatic hydrocarbon; TPH = total petroleum hydrocarbon

Figure B.5
Summary of State Regulatory Requirements for Total Petroleum Hydrocarbons in Soil at Fuel-release Sites
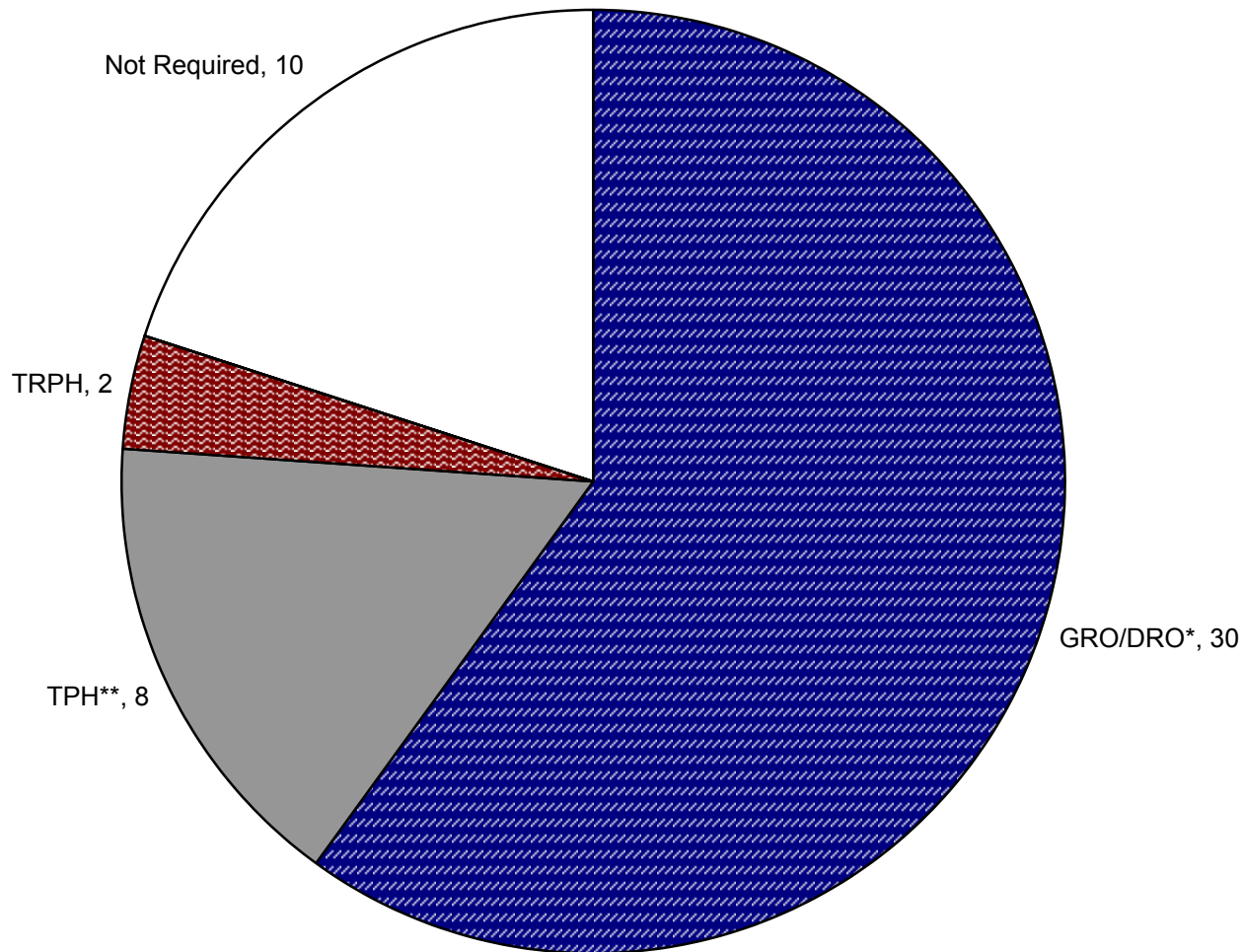
*California also requires TRPH at diesel sites. Tennessee requires that analyses consist of GRO and EPH.

**Two states utilize a state-specific method to determine TPH; six states utilize a state-specific method to determine TPH as VPH/EPH or TEH.

Note: GRO = gasoline-range organics; DRO = diesel-range organics; TPH = total petroleum hydrocarbon; TRPH = total recoverable petroleum hydrocarbons; VPH = volatile petroleum hydrocarbons; EPH = extractable petroleum hydrocarbons; TEH = total extractable hydrocarbons

Figure B.6
Summary of State Regulatory Requirements for Total Petroleum Hydrocarbons
in Ground Water at Fuel-release Sites
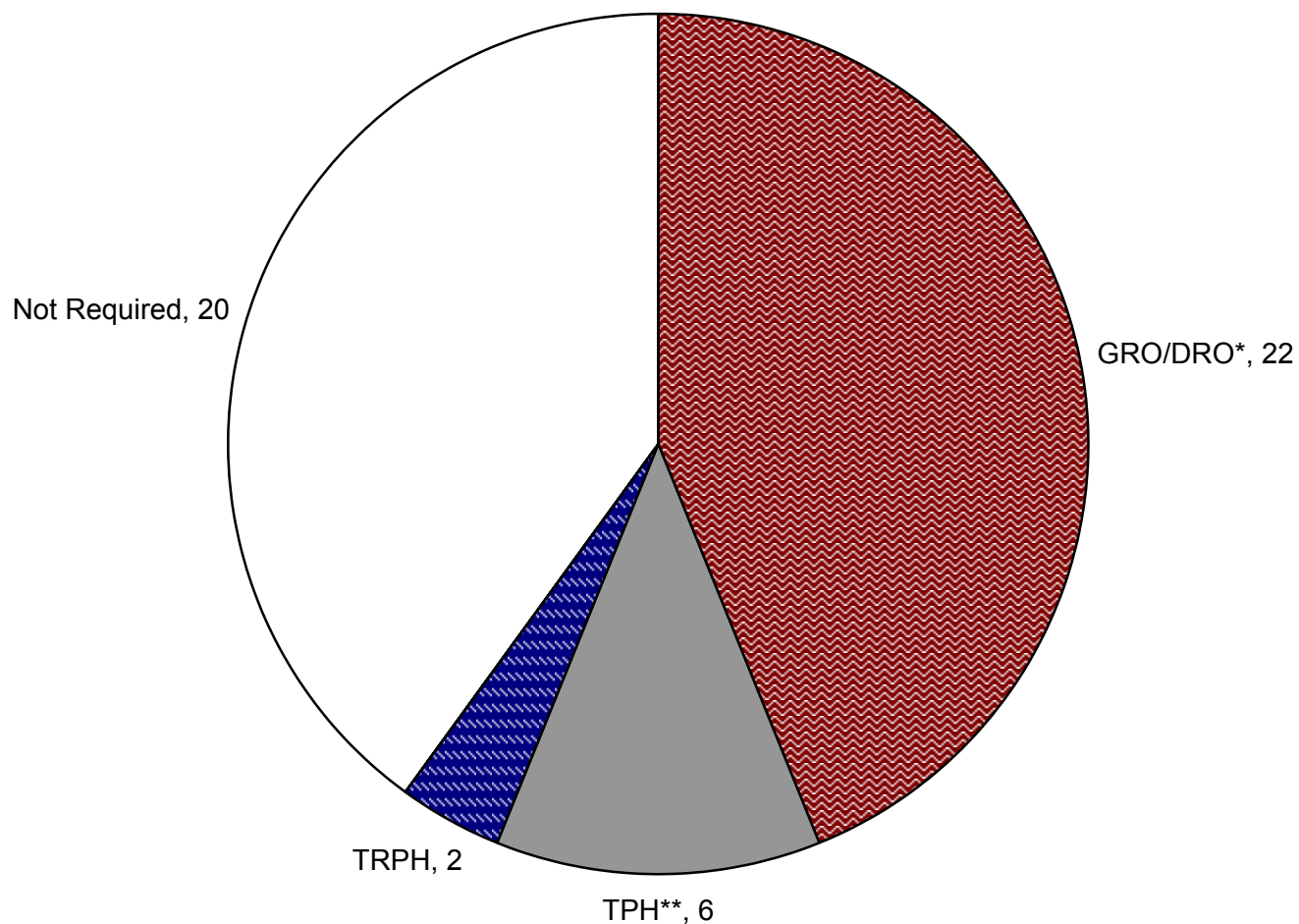
*California also requires TRPH at diesel sites. Tennessee requires that analyses consist of GRO and EPH.
**Two states utilize a state-specific method to determine TPH; four states utilize a state-specific method to determine TPH as VPH/EPH or TEH.
Note: GRO = gasoline-range organics; DRO = diesel-range organics; TPH = total petroleum hydrocarbon; TRPH = total recoverable petroleum hydrocarbons; VPH = volatile petroleum hydrocarbons; EPH = extractable petroleum hydrocarbons; TEH = total extractable hydrocarbons

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Figure B.7
Summary of State Regulatory Requirements for Gasoline Additives in
Soil at Fuel-release Sites
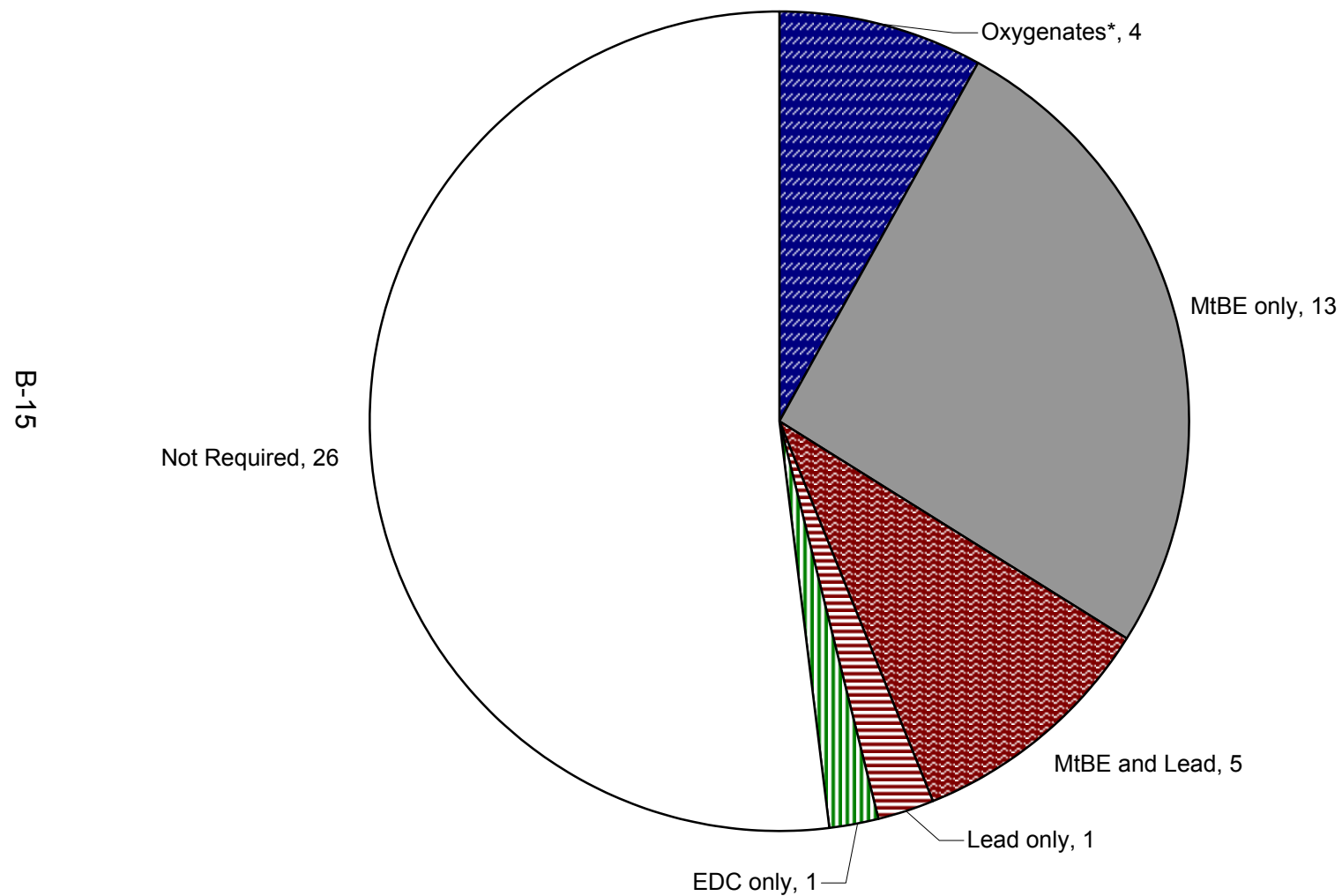
*Three states require analysis for MtBE, lead, EDB, and EDC. California requires analysis for several different oxygenates that may be determined on a site-by-site basis.

Note: MtBE = methyl tert-butyl ether; EDB = ethylene dibromide; EDC = ethylene dichloride

Figure B.8
Summary of State Regulatory Requirements for Gasoline Additives
in Ground Water at Fuel-release Sites
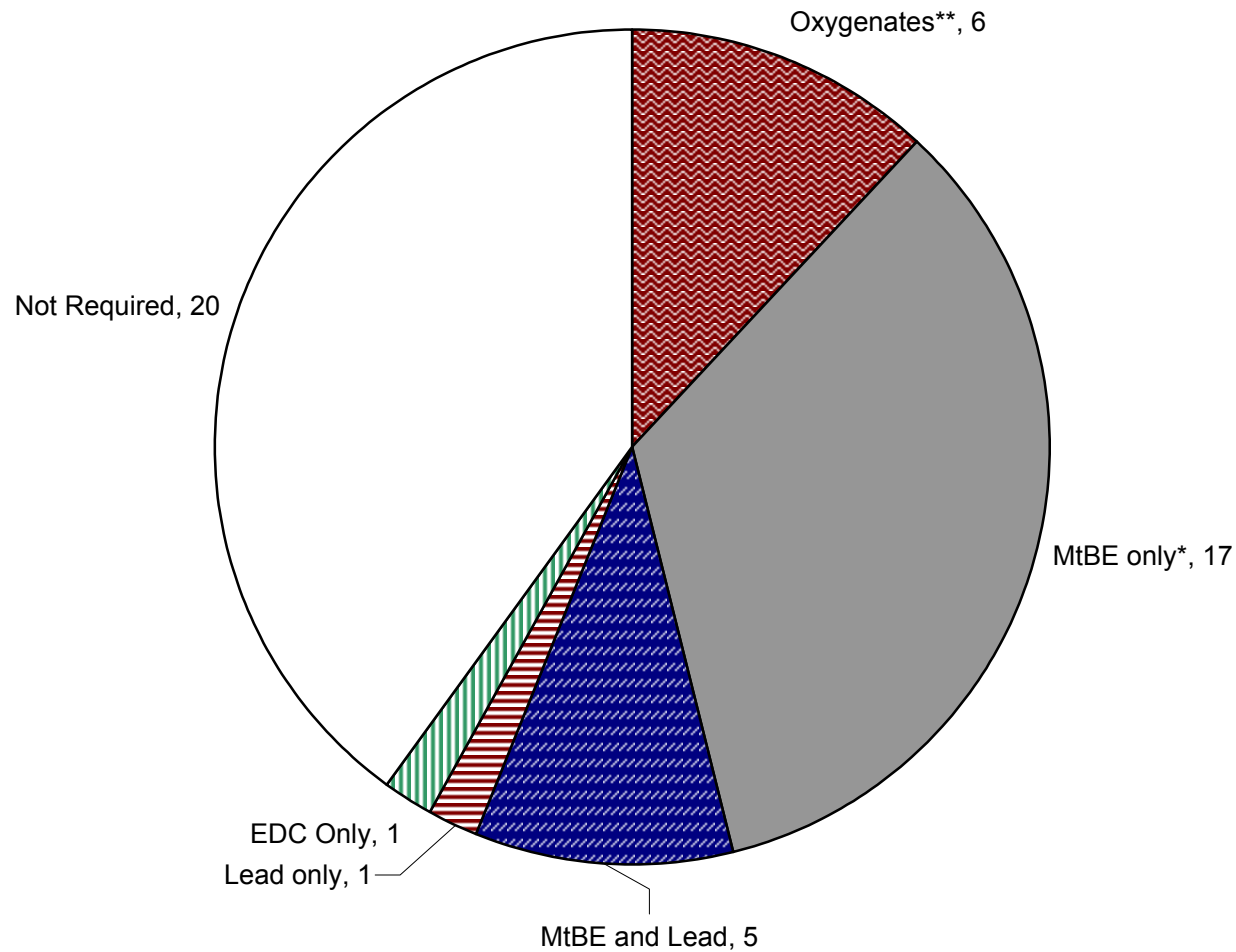
*South Carolina also requires analysis for EDB.

**Five states require analysis for MtBE, lead, EDB, and EDC. California requires analysis for several different oxygenates that may be
determined on a site by-site basis. New Jersey specifically requires analysis for TBA.

Note: MtBE = methyl tert-butyl ether; EDB = ethylene dibromide; EDC = ethylene dichloride; TBA = tert-butyl alcohol

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APPENDIX C

COMPONENTS OF CONCEPTUAL SITE MODELS FOR FUEL-RELEASE SITES

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C.0   INTRODUCTION

As described in Section 2.1.2, United States Environmental Protection Agency (USEPA) guidance provided in *Use of MNA at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (USEPA, 1999), indicates that site characterization and development of a conceptual site model (CSM) are an essential processes that should be completed prior to evaluating the efficacy of monitored natural attenuation (MNA) as a remedial alternative. The conceptual site model (CSM) for a fuel-release site is a three-dimensional representation of the earth materials in the area of interest, and the processes that govern the occurrence, transport, and fate of contaminants of concern (COCs). The complexity of the CSM will vary by site; complex sites may require assemblage and synthesis of more information than relatively simple sites. The CSM should focus on information that is relevant to addressing the site-specific goals and objectives. For example, it may not be necessary to define the regional physiography and the stratigraphy to a depth of 300 feet below ground surface (bgs) for a small underground storage tank (UST) site with a 300-foot-long dissolved benzene, toluene, ethylbenzene and xylene isomers (BTEX) plume that is wholly contained within the uppermost 50 feet of the subsurface. Although the complexity of the CSM will be site-specific, there are three common elements of all CSMs:

- Definition of the source and affected media;

- Contaminant release mechanisms, potential migration pathways (e.g., ground water, soil, soil gas, surface water), attenuation mechanisms (e.g., volatilization, biodegradation), and exposure routes (e.g., inhalation, ingestion, dermal contact); and

- An understanding of current and potential future receptors (see Section 2.3.3 for additional details).

Each of these elements is discussed in more detail in Sections C.1 through C.4.

The CSM, which is developed using available geologic, hydrogeologic, hydrologic, geochemical, climatological, biological, and physicochemical data for the site, provides the basis for understanding the nature, extent and movement of fuel-related contaminants at the site, and incorporates and organizes the available information into a framework that can be used to guide site investigations and remediation activities. Without adequate development and understanding of the CSM, subsequent activities will not generate interpretations or conclusions that can be used with confidence. Development of the CSM begins concurrently with initial assessment and scoping activities, and continues throughout the data collection/analysis and remediation phases. The CSM should be continually updated and refined as new information is obtained.

C.1   INFORMATION REQUIREMENTS

To develop an accurate CSM, the following information should be considered for its relevance to a specific site:

1. Definition of the source and affected media
   - Release mechanism(s) (e.g., leaking pipeline or UST)
   - Type(s) of fuel released

<div align="center">C-1</div>

- Distribution of the released fuel in the subsurface (i.e., occluded, sorbed, vaporized, dissolved, and/or light non-aqueous phase liquid (LNAPL)

- COC concentrations and lateral and vertical extent of contamination in the source area

2. Definition of migration pathways and exposure routes

- Regional physiography, geology, and hydrogeology

- Site-specific geology and hydrogeology

- Local climatic conditions

- Local surface drainage patterns and surface-water/ground-water interactions

- Contaminant migration directions and rates

- The existence of preferential migration pathways and barriers to migration

- Natural attenuation potential of the vadose and saturated zones and the contaminant fate process(es) occurring at the site (e.g., biodegradation, sorption, volatilization)

3. Definition of current and potential future receptors

- Land use plans

- Locations of occupied buildings

- Presence of ecological receptors (e.g., plants, mamals, fish)

It is necessary to collect and integrate all of above-listed information that is relevant to the site of interest. Regional and local information can be obtained from a variety of sources, including the United States Geological Survey (USGS), the United States Army Corps of Engineers, the Soil Conservation Service, the USEPA, state geological surveys, state regulatory agencies, state departments of agriculture, university libraries, professional organizations, technical journals, and the internet. Site-specific information can be obtained from existing environmental reports, geotechnical/geologic/hydrogeologic reports, current and historical aerial photographs and topographic maps, and interviews with current or former site workers. Each of the elements of a CSM are more fully described in Sections C.2 through C.4.

C.2   DEFINITION OF THE SOURCE AND AFFECTED MEDIA

A valid CSM that delineates the distribution of contaminants in the subsurface is essential for understanding potential receptor exposure risks and developing a credible and effective remedial action plan. For example, a valid conceptual site hydrogeologic model that delineates the distribution of contaminants in the subsurface is essential for understanding how source-reduction techniques will impact ground-water contaminants. As described in Downey *et al.* (1999), fuel contamination may be present in the subsurface in several forms:

- **Occluded** - In soils, LNAPL often exists at concentrations that are less than residual saturation. This fuel LNAPL is present as small droplets trapped between soil particles. Occluded LNAPL represents the majority of the contaminant mass at most sites.

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- **Sorbed** - This is contamination reversibly bound to the surface of soil particles, and may represent a more significant mass at many sites than dissolved contamination, but usually less mass than occluded LNAPL.

- **Continuous free phase** - This is the free-phase product, or recoverable (mobile) LNAPL, present at sufficiently high concentrations to form continuous layers that will flow into a monitoring well. Mobile LNAPL normally represents less than 10 percent of the LNAPL mass present at most sites, and rarely exceeds 33 percent.

- **Soil gas** - The fraction of contamination in this phase depends upon the vapor pressure of the fuel and site-specific conditions. With a highly volatile fuel such as gasoline, 1 or 2 percent of the total hydrocarbon mass may reside in the soil gas.

- **Dissolved** - The fraction of fuel contamination dissolved in ground-water or in pore water in the vadose zone generally represents less than 1 percent of the total mass, and is dependent on the solubility of the fuel constituents, the age of the spill, and site hydrogeologic conditions.

Contamination can be present in the vadose zone and/or the saturated zone, depending on the depth at which the fuel release occurred. Generally, a major fraction of the LNAPL contaminant mass resides above the seasonal low water table. At most sites, the only mechanism for transport downward to the water table is the leaching of dissolved hydrocarbons in infiltrating precipitation or irrigation waters. Leaching is minimized when soils are covered with impermeable materials and/or are located in low-precipitation regions. Two exceptions are 1) when the regional water table has been lower in the past than it is now and 2) when fuels leak from sources that are installed below the seasonal low ground-water level.

The fuel hydrocarbon "smear zone" is defined as the layer between the permanent vadose and saturated zones. This is the zone within which the water table fluctuates seasonally, and where capillary forces maintain near-saturated conditions. The thickness of the smear zone is site-specific and is based on soil characteristics and seasonal water table fluctuations. At most sites, the water table fluctuates only a few feet. The thickness of the capillary fringe also will depend on site-specific conditions. In a coarse, sandy soil, the capillary fringe may be quite thin (e.g., a few inches thick); in a clay soil, the capillary fringe may extend several feet above the water table.

In summary, at a typical fuel release site, the contaminant mass will be distributed as occluded, sorbed, free phase, vapor phase, and dissolved forms. The largest percentage of contaminant mass typically resides within the vadose zone, smear zone, and/or capillary fringe as residual (sorbed or occluded) LNAPL. Mobile LNAPL will typically contain no more than 10 to 30 percent of the contaminant mass (Downey *et al.,* 1999).

The CSM should describe the fuel release in terms of type(s) of fuel, the date or time period of the release, the quantity of material involved, and the location. This information often is most readily obtained from site personnel or the agency responsible for regulatory oversight.

Knowing the type of fuel released provides insights into potential receptor exposure risks and the fate and transport of COCs in the subsurface. For example, at the site of a JP-4 jet fuel spill, benzene in ground-water may represent the chemical and receptor exposure pathway of greatest concern. Due to the relatively limited solubility of benzene in water (relative to its solubility in

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JP-4), the mass of dissolved benzene typically is quite small. It is not uncommon to find that less than 1 percent of the mass of benzene at a site is dissolved in ground-water, while more than 95 percent of the benzene mass often is retained in free product or fuel residuals trapped in soils near the source of the product release (AFCEE, 1998).

It should be noted that the mass of BTEX present in free product or as fuel residuals can be substantially reduced over time through natural weathering. For example, the average first-order weathering rate for total BTEX at five JP-4 sites was estimated to be approximately 12 percent per year (Parsons, 2003). The CSM should evaluate the fuel weathering rates to determine the expected persistence of elevated contaminant levels. LNAPL weathering rates can be estimated via collection of LNAPL samples from the same locations over time (typically at least a few years).

In summary, site contamination should be fully characterized such that:

- COCs have been identified;

- The presence or absence of mobile LNAPL and the thickness of any product smear zone bordering the water table have been determined;

- Contaminant concentrations in all impacted media (e.g., soil [including product smear zones], water, soil vapor, and surface water) are known; and

- The lateral and vertical extent of contamination has been determined.

The contaminant levels should be compared to applicable cleanup standards for each medium (see Section 2.2.1 for a discussion on the use of site-specific, risk-based cleanup levels).

C.3 RELEASE MECHANISMS, MIGRATION PATHWAYS, ATTENUATION PROCESSES, AND EXPOSURE ROUTES

As shown on Figures 2.2 and 2.3, potential fuel-release mechanisms at typical USAF sites include direct release of contaminants into soil or ground water. As shown on Figure 3.1, potential migration pathways include airborne transport of contaminated particulates or volatilized contaminants, overland flow of contaminated runoff water, downward leaching of contaminants into the vadose zone and possibly to the water table, migration of dissolved contaminants within the ground-water system in response to hydraulic gradients, and transport within surface streams that become contaminated as a result of ground-water discharge or surface runoff. Potential attenuation mechanisms that affect contaminant transport and concentrations during migration include non-destructive processes such as sorption, volatilization, dispersion, dilution, photodegradation, and volatilization; and destructive mechanisms (i.e., biodegradation). Exposure routes by which potential receptors can contact contaminants include incidental ingestion of contaminated soil or water, dermal contact, and inhalation of contaminated particulates or volatilized contaminants.

Evaluation of potential migration pathways and attenuation mechanisms involves understanding:

- The local climatic conditions that may influence contaminant migration (e.g., precipitation, evapotranspiration);

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- The environmental setting of the site, including physiography, geology, hydrogeology, surface-water hydrology, and surface-water/ground-water interactions; and

- The natural attenuation potential of the vadose zone and ground-water system, which involves defining the organic carbon content of vadose- and saturated-zone matrix materials, and the relevant ground-water geochemistry.

The various elements of this portion of the CSM are discussed in the following subsections.

C.3.1 Climate

The CSM should evaluate the effect of local climatic conditions on contaminant movement, including such factors as precipitation and evapotranspiration rates, temperature, and prevailing wind direction and speed. Precipitation can influence contaminant movement by transporting contaminants laterally via surface runoff or vertically via infiltration through vadose zone soils. In addition to determining precipitation rates, the CSM should at least qualitatively evaluate the amounts of precipitation that 1) infiltrate the vadose zone and recharge the ground-water system, 2) travels overland via surface run-off, and 3) is lost to evapotranspiration. High winds can transport contaminated particulates downwind of a site, potentially impacting downwind properties and receptors.

Climatic information can be obtained from the National Climatic Data Center at http://www.ncdc.noaa.gov/oa/ncdc.html, the National Oceanic and Atmospheric Administration at http://lwf.ncdc.noaa.gov/oa/climate/research/cag3/cag3.html, and regional climate centers at http://www.wrcc.dri.edu/rcc.html. In addition, detailed site-specific weather data, if required, can be collected using a rain gauge and/or a more sophisticated onsite weather station. However, in most cases this should not be necessary.

C.3.2 Regional Physiography, Geology, and Hydrogeology

A CSM should describe the regional physiographic, geologic, and hydrogeologic setting of the site if the current or potential future size of the impacted area is sufficiently large to benefit from the regional perspective.

C.3.2.1 Regional Physiography

Identification of the physiographic province within which the site is located may be relevant and useful because the landforms, stratigraphy, and geologic structures within a province are generally similar (Stone, 1999). Therefore, identification of the physiographic province may provide insights into local conditions that may influence the occurrence, migration, and fate of contaminants. The USGS has identified 10 physiographic provinces in the contiguous United States that include the Pacific Mountain System, Columbia Plateau, Basin and Range, Colorado Plateau, Rocky Mountain System, Laurentian Upland, Interior Plains, Interior Highlands, Appalachian Highlands and Atlantic Plain provinces. A web site developed by the USGS and the National Park Service includes a map showing the area of each province (www.aqd.nps.gov/grd/usgsnps/province/province.html). The web site includes information on each province, including the geology, age of formations, subprovinces, maps, and photographs.

C.3.2.2 Regional Geology

The stratigraphic sequence present in the vicinity of the site should be described to the extent that it is relevant to the site. Specifically, all stratigraphic units that may be impacted by contamination, or that could influence contaminant migration, should be identified and described. For example, it would be relevant to describe the presence of a regional, confined, drinking-water aquifer located 100 feet below the impacted surficial aquifer if pumping from the confined aquifer could potentially draw dissolved contaminants into deeper zones. Given that fuel is an LNAPL that is less dense than water, dissolved fuel contamination will be limited to the upper portion of the saturated zone in most instances, unless the presence of natural or pumping-induced downward hydraulic gradients promote downward contaminant migration. Presentation of a figure depicting a generalized stratigraphic column and/or hydrogeologic cross-section of the area will be useful in many instances.

The CSM should include the formal nomenclature, thickness, areal extent, and age of each stratigraphic unit that is potentially relevant to the site. Important structural features (e.g., major fault zones, dipping rock beds) and major landforms (e.g., depositional features) within the site vicinity also should be considered to the extent that that they may influence the migration and fate of contaminants. The discussion should include any information that may be relevant to ground-water movement and contaminant migration, such as the orientation of faults and joints that may constitute preferential migration pathways. Topographic maps, aerial photographs, boring logs, and photographs can also be reviewed to obtain an understanding of the regional setting.

C.3.2.3 Regional Hydrogeology

The aquifers and aquitards that comprise the regional ground-water system in the vicinity of the study site should be identified, including their lithology, thickness, extent, and degree of hydraulic interconnection. The geologic information described in Section C.3.2.2 can be used to identify the geologic controls on the occurrence, movement, and quality of ground-water. Pertinent hydrogeologic information such as depth to ground-water; presence of perched ground-water zones; recharge and discharge areas, mechanisms, and rates; whether the various water-bearing zones are unconfined, semi-confined, or confined; relative permeabilities; and ground-water flow directions and rates also should be described. Pertinent chemical information such as the general quality of the groundwater (e.g., salinity, total dissolved solids content) which affects its usage also may be useful to identify.

Most basic hydrogeology textbooks (e.g., Fetter, 1994; Freeze and Cherry, 1979) discuss the concepts relevant to characterizing the hydrogeology of an area (e.g., characteristics of recharge and discharge areas). In addition, Stone (1999) provides an overview of the basic components and tasks of a sound hydrogeologic study. According to Stone (1999), the most important knowledge concerning the conceptual hydrogeologic model can be gained by answering the following 10 basic questions:

1. What is the aquifer?
2. What are its geologic and hydrologic properties?
3. How deep is the regional saturated zone?
4. Where does the water come from?

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5. Which way does the water flow?

6. What is the hydraulic gradient?

7. How and where does the water come back to the surface?

8. What is the quality of the water?

9. Are there any contaminants?

10. What are the geologic controls on the hydrologic system?

C.3.3   Site-specific Geology and Hydrogeology

The discussion of the site-specific geology and hydrogeology should focus on the same elements identified in Sections C.3.2.2 and C.3.2.3; however, the discussion should focus specifically on the characteristics of the fuel-release site. In many cases, more detailed information will be available for the site than for the region due to the performance of site characterization activities related to the contaminant release. All available information should be used to assemble a detailed, site-specific CSM that highlights the features that influence and control the movement and transformation of contaminants in the subsurface, including:

- Stratigraphy (e.g., name, age, texture, thickness, depth, and lateral extent of each potentially impacted stratigraphic unit, aquifer, and aquitard);

- Relevant geologic structures such as faults, joints, and folds;

- Heterogeneity and anisotropy;

- Ground-water recharge and discharge;

- Ground-water depth;

- Ground-water flow directions and rates;

- Relatively permeable zones that constitute preferential migration pathways, including underground utility corridors;

- The influence of pumping or injection wells and other anthropogenic features on ground-water flow and contaminant migration;

- Importance of advective versus diffusive contaminant transport; and

- Ground-water/surface-water interactions.

Many of the relevant features listed above can (and should) be depicted in representative figures including hydrogeologic cross-sections and potentiometric surface maps.

The CSM must evaluate the interrelationships of geologic materials and processes with water, especially groundwater, and their influence on contaminant fate and transport at the site. Hydrogeologic information from the National Water Data Storage and Retrieval System maintained by USGS can be accessed by authorized users by means of an on-line computer retrieval system known as the Ground-water Site Inventory file.

C.3.4   Surface-water Hydrology and Surface-water/Ground-water Interaction

Surface runoff patterns and discharge points should be identified and described because runoff provides a mechanism for contaminant transport. Steams flowing through a contaminated area can also provide a contaminant transport mechanism. For surface-water bodies on or near the site, the CSM should evaluate potential impacts to the water body and to any sensitive ecological receptors that may reside in or use the water body based on distance of the water body from the contamination, and whether the water body is hydraulically downgradient, cross-gradient, or upgradient of the contaminated area.

Information on streams and rivers should include the following: source of water; perennial or ephemeral; losing or gaining; average volumetric flow rate, and regulatory classification (e.g., drinking-water source). The use of the stream or river should be described, as well as the use of downstream bodies of water into which the stream or river discharges. Other surface water bodies (i.e., lakes, ponds, swamps, wetlands) should be described in terms of size, source of water, depth and use (e.g., recreational, consumptive). Available water-quality data for all surface water should be evaluated. Maps or aerial photographs can be used to understand surface-water flow systems.

A stream may gain or lose water along its course, depending on the depth of the stream with respect to the water table. When the water table is shallow, the stream may gain water via ground-water discharge. It is important to assess the potential for contaminant plumes to migrate and discharge to a surface-water body. When the water table is below the bottom of the stream, streams tend to lose water to the unsaturated zone. Under such conditions, the groundwater may underflow the stream. Alternatively, if a ground-water mound is formed beneath the losing stream due to enhanced recharge, it may form a hydraulic barrier to ground-water flow, resulting in at least localized diversion of groundwater migrating beneath the stream.

C.3.5   Geochemistry and Natural Attenuation Potential

As described in Appendix A, ground-water geochemistry may influence, or be influenced by, biodegradation processes. As discussed in Section 1.2, geochemical data of the proper type indirectly demonstrate the type(s) of natural attenuation processes active at the site. Therefore, obtaining the proper geochemical data is an important aspect of a CSM for a fuel-release site. Geochemical parameters of interest include electron acceptors, metabolic byproducts, other indicators of redox conditions, and general water-quality parameters. Evaluation of background measurements of various geochemical parameters can provide insight to the general quality of water from each major stratigraphic unit. For example, naturally aerobic (oxidizing) aquifers are generally desirable as water-supplies, while anaerobic (reducing) aquifers may have natural taste and odor issues that make them less desirable, or in some cases unsuitable, water supply units. Measurement and interpretation of redox indicator parameters are discussed more fully in Section 3.4.3.4 and Appendix A. Use of these data to support the MNA evaluation is discussed in Section 4.2.2.2.

The migration of contaminants in the subsurface is retarded due to contaminant sorption onto aquifer matrix materials, especially organic carbon. Therefore, the organic carbon content of aquifer matrix materials should be measured in multiple "background" locations of each contaminated unit to allow calculation of retardation factors for input into fate and transport models, as discussed in Sections 3.4.2.3 and A.4.2.3 (Appendix A).

C.3.6 Exposure Routes

Exposure routes for commercial/industrial areas that are characteristic of fuel-release sites at USAF installations include incidental ingestion, dermal contact, and inhalation. These exposure routes are briefly discussed in Section 2.3.3 of this document and illustrated on Figures 2.2 and 2.3. Performance of an exposure pathway analysis is described in greater detail in the following paragraphs. The CSM should incorporate sufficient information to perform this type of analysis in order to evaluate risks posed by site contamination.

The risk-based paradigm, established by the USEPA as part of the Superfund program, consists of four basic technical elements that progress logically to a quantitative evaluation of the site-specific risks to human health and the environment. The elements required for risk-based site assessments are:

- Hazard identification,

- Exposure assessment,

- Toxicity assessment, and

- Risk characterization.

Hazard identification consists of identifying site-specific constituents of potential concern (COPCs) and contaminated media that represent potential threats to human health and the environment. This identification is accomplished by reviewing the available site characterization information, and evaluating the hazard potential of detected constituents, based on their known effects to human and/or environmental receptors. This evaluation establishes the list of COPCs that will form the basis for subsequent risk-based analysis. As discussed in Section A.2, the compounds of concern at fuel sites typically include BTEX, polycyclic aromatic hydrocarbons (PAHs), and fuel additives (e.g., methyl tert-butyl ether [MtBE]).

The *exposure assessment* is used to develop an understanding of the movement of constituents of potential concern from contaminated media at the site, through the environment, to a point of contact with human or environmental receptors. Site-specific factors examined in the exposure assessment include identification of contaminated media, evaluation of the physical and chemical properties controlling the movement and fate of site-specific contaminants, and a qualitative assessment of the rates and directions of chemical migration. When COCs include volatile compounds (e.g., BTEX, MtBE), the exposure assessment should include an evaluation of soil gas and/or indoor air within and adjacent to nearby structures.

The toxicological effects of site-related constituents and contaminated media on potential receptors are evaluated as part of the *toxicity assessment*. The effects of concern include acute and chronic effects, and address both carcinogenic and non-carcinogenic toxicological endpoints. This information is used to estimate the toxicological effect to a receptor that could result from a specific intake ("dose") of the constituent.

Risk characterization integrates the information from the hazard identification, exposure assessment, and toxicity assessment to develop a quantitative evaluation of the risk associated with a site. The risk characterization thus begins with the identification of site-related constituents, projects their release and movement in the environment, estimates their uptake by

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potential human and environmental receptors, and evaluates the possible toxicological effects of these chemical "doses" on receptors as a measure of potential risk

As described in the Superfund Public Health Evaluation Manual (USEPA, 1986) and in Section 2.3.3 of this protocol addendum, an exposure pathway consists of four necessary elements:

1. A source and mechanism of chemical release to the environment;

2. An environmental transport medium for the released chemical;

3. A point of potential contact for human or environmental receptors with the contaminated medium (referred to as the exposure point); and

4. A receptor exposure route at the exposure point.

An exposure pathway is complete when all four elements are present, and is incomplete when one or more elements are missing. Exposure estimates can only be calculated for completed exposure pathways.

Two general pathways – surface pathways and subsurface pathways – can function as potential routes of chemical migration from source areas to other media, and/or to potential receptors. Surface transport mechanisms can include surface-water runoff; entrainment and transport of soil (as sediment) during precipitation events; overland flow from springs and seeps; airborne transport of fugitive dusts, aerosols, or vapors; and anthropogenic transport (e.g., excavation and removal of soil). Subsurface transport mechanisms can include movement of site-related constituents as a free phase ("non-aqueous phase"), as a dissolved phase in infiltrating precipitation, or in water within the saturated zone; and as a vapor phase in unsaturated pore spaces.

The four environmental media in which transport of site-related constituents can occur, potentially resulting in exposure of susceptible populations to chemicals, are ground water, surface water and sediment, soil, and air. Numerous factors can affect the migration and potential bioavailability of chemicals, including:

Ground Water	Surface Water and Sediment
Direction of flow	Flow velocity
Hydraulic gradient	Slope
Hydraulic conductivity	Discharge rate
Chemical partitioning	Sediment load

Soil	Air
Soil chemistry	Temperature
Degree of saturation	Wind velocity
Chemical partitioning	Chemical volatility

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C.4   DEFINITION OF CURRENT AND POTENTIAL FUTURE RECEPTORS

Examples of potential human receptors include employees working at fuel-release sites, people who live or work near the site, and individuals who obtain drinking water from an impacted water-supply well. Other potential receptors include public and private wells, well-head protection areas, threatened or endangered species or habitats, and wetlands.

Identifying human receptors at a particular site involves defining the current and potential future land uses. Determining current and future receptors and land use is more fully discussed in Section 2.3.2 of this document. Given that most fuel-release sites at United States Air Force (USAF) installations are located in commercial/industrial areas, the potential for significant impact to ecological receptors is low. However, the potential for this to occur should be evaluated on a site-specific basis. The most likely scenario for impact to ecological receptors is via discharge of contaminated groundwater to a surface-water body.

If the fuel compounds released at a site contain substantial concentrations of volatile compounds (e.g., benzene), the existence of preferential pathways for vapor migration, including underground utility corridors or permeable soil horizons, should be evaluated. If buildings are located near the source area, or fuel vapors are detected near a building, indoor air quality should be evaluated to identify whether potentially toxic or explosive vapor concentrations are present, especially in basement areas (see Section 3.3.2.3.2).

C.5   REFERENCES

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APPENDIX D
SITE CHARACTERIZATION METHODOLOGIES

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D.0   INTRODUCTION

Traditionally, site characterization has been conducted using a phased engineering approach (mobilize staff and equipment to site, collect samples to ship to a lab, wait for results to be analyzed and interpreted, and repeat the process to collect more samples until an adequate level of characterization is achieved). While the phased approach is widely accepted and used at many fuel-release sites across the country, an increasing number of fuel-release characterizations are using on-site analysis to screen samples as part of an expedited (or accelerated) site characterization process, as described for fuel-release sites by the United States Environmental Protection Agency (USEPA, 1997a) and the American Society for Testing and Materials (ASTM, 1998).

Office of Solid Waste and Emergency Response (OSWER) recommends a three-part, or "triad", approach for implementation of expedited site characterization that is described by USEPA (2001a, 2001b) and Crumbling *et al*. (2003). In summary, the triad approach uses systematic planning, dynamic work plans, and on-site analytical tools to plan and implement data collection and technical decision-making at hazardous waste sites. *Systematic planning* involves the creation of a conceptual site model (CSM) as a planning tool to organize what is already known about the site and to help the team identify what more must be known to make the decisions that will achieve the project's goals. A *dynamic work plan* helps sampling teams make technical decisions in the field by utilizing a regulator-approved decision-tree. The work plan is supported by the rapid turnaround of data that are collected, analyzed, and interpreted in the field through the use of on-site analytical 'screening' tools that offer the advantage of providing 'real-time' data. In addition to providing 'real-time' data, *onsite analytical tools* (e.g., field screening techniques) are likely to be less expensive (per sample) at sites where a relatively large number of samples are required. The ramification of a lower cost per sample is that field-screening analysis techniques allow for analysis of a larger number of sampling points (i.e., a denser sampling grid), relative to fixed-based laboratory analysis, for the same overall cost (e.g., Crumbling *et al*., 2003).

Note that, for the purpose of establishing regulatory compliance to specific standards, fixed-based laboratory methods, which typically offer more definitive results and lower method detection limits than field-screening techniques, will still be required for those samples collected in locations identified as 'critical' through the field screening process (USEPA, 2001a). For additional information on the USEPA triad approach, including copies of the references cited in this appendix, visit the USEPA's *Characterization and Monitoring: The Triad* webpage at http://www.epa.gov/swertio1/triad/.

Regardless of whether site characterization activities are performed in a phased or expedited manner, chemical concentration characterization of both the contaminant source area (Section D.1) and, if impacted, ground water (Section D.2), will be required as part of the site characterization process and any concurrent or subsequent monitored natural attenuation (MNA) evaluations. The following text provides a summary of techniques that are recommended for sampling various media at fuel-release sites. Section D.3 is provided as a brief summary of QA/QC requirements for a typical fuel-release site sampling program.

D.1   SOURCE CHARACTERIZATION METHODOLOGIES

During source characterization activities, sampling of soil, soil vapor, and (if present) mobile light non-aqueous phase liquid (LNAPL) will be required to characterize the nature, extent, and weathering characteristics of the source. Methodologies for sampling soil, soil vapor, and mobile LNAPL at fuel-release sites are described in Sections D.1.1, D.1.2., and D.1.3., respectively.

D.1.1   Soil Sampling

D.1.1.1   Elements of a Soil Sampling Program

Characterizing contaminated soils resulting from a fuel release presents a number of challenges due to the inherent heterogeneity of soils. For example, the source area may be limited in areal extent at some fuel-release sites, and could be potentially missed by a sampling program that uses a sample grid spacing that is significantly larger than the source area. Conversely, a grid sample spacing that is too fine at a site with a large area of soil contamination could result in collection of more data than is really needed for characterization and/or MNA evaluation purposes. It is important to remember that the main goal of a soil evaluation is to determine, for each release, the distribution of contamination in the soil matrix, and to delineate the extent of contamination that exceeds the applicable regulatory criteria. The following elements (modified from Connecticut Department of Environmental Protection, 2000) should be helpful when designing a site-specific soil sampling program:

- Document the objective of each sample location;

- Verify microstratigraphic details relevant to subsurface contaminant migration with continuous geologic data collection (e.g., continuous casing or direct push measurements) as much as possible;

- Include targeted sampling for identified preferential contaminant migration pathways;

- Focus on any soil, soil moisture, or water table zones or interfaces that may inhibit gravity-driven migration of LNAPLs;

- Use field screening for dynamic real-time feedback to refine sampling locations;

- Consider the need for soil sampling below the water table if the source extends into the saturated zone (i.e., delineate the vertical extent of a free product smear zone);

- Consider the need for collecting soil samples to facilitate contaminant fate and transport analysis (e.g., total organic carbon [TOC] as described in Section 3.4.2.3, and bioavailable iron, as described in Section 3.4.3.4.3);

- If a statistical evaluation is planned, collect a sufficient number of samples to perform statistically valid calculations;

- When conducting random sampling of an area, estimate the minimum size hotspot which the sampling program will detect and compare this estimate with the CSM-predicted release size for appropriateness of soil spacing; and

- Recognize that older fuel-releases and/or from leaking USTs may show little contamination in the first 6 inches below ground surface due to volatilization and other weathering mechanisms, even though deeper soils may be heavily contaminated. Surface samples may thus underestimate the extent of a problem.

D.1.1.2   Defining Objectives

Before sampling, it is critical to identify and understand the purpose for sampling and how the resultant data will be used (Karklins, 1996). One systematic approach to defining sampling objectives is the data quality objective (DQO) approach described in Sections 3.2.3 and 5.2. In general, and as described in USEPA (1995a), sampling objectives for soils may include:

- Evaluate current or potential threats to human health or the environment;

- Locate and identify potential sources of contamination;

- Define the extent of contamination;

- Determine treatment and disposal options; and

- Document the attainment of cleanup goals.

D.1.1.3   Quality Control

A primary goal of any soil sampling program is to collect samples which yield analytical results that accurately depict site conditions during a given time frame. A properly designed sampling plan should consider and account for site variation. Examples of site variation include changes (in space and time) of both the type and concentration of contaminants throughout a site. For a sampling program to be considered representative, sampling should allow for identification and quantification of this variation. For example, a sampling grid with relatively large distances between sampling points or a biased sampling approach may allow significant contaminant trends to go unidentified (USEPA, 1995a). Quality assurance (QA) objectives, including collection of sufficient quality assurance/quality control (QA/QC) samples, should be considered when designing the sampling program (see Section D.3).

D.1.1.4   Soil Sampling Design Plan

Selecting sampling locations for field screening or laboratory analysis involves choosing the most appropriate sampling approach. Representative sampling approaches include judgmental, random, stratified random, systematic grid, systematic random, search, and transect sampling. A representative sampling plan may combine one or more of these strategies, which are defined in USEPA (1995a). At a typical United States Air Force (USAF) fuel-release site, the source(s) of contamination are known to some extent based on historical knowledge of site use (e.g., underground storage tank [UST], underground pipeline, Fire Training Area). Therefore, a judgmental sampling approach that is based on the known locations and characteristics of the release would typically be appropriate for most fuel-release sites. An appropriately designed

judgmental sampling approach could then be used to investigate the magnitude and extent of the contamination (e.g., site characterization) and to confirm the effectiveness of a remedial action (e.g., remedy evaluation).

D.1.1.5 Soil Sampling Techniques

Subsurface soil sample collection intervals can be divided into one of three broadly defined categories: surface and shallow (0-10 feet), medium (10-100 feet), and deep (100 or more feet) explorations. Manual soil sampling techniques (e.g., hand augering) are potentially useful and cost-effective when sampling shallow depths of the soil column. When sampling deeper intervals however, manual methods are typically labor intensive, time consuming, and/or physically impossible. Conventional drilling and direct-push techniques (DPT) provide quicker access to both medium and deep interval soils, and can be implemented to better assess the stratigraphy of soils. **Table D.1** contains descriptions of several soil sampling techniques and the respective depths for which they are commonly used. Conventional drilling techniques for geologic and environmental investigations have been well-described by ASTM and others, and will not be explicitly described in additional detail here. Additional information on direct-push platforms is included below, as these relatively new techniques may offer a cost-effective alternative to conventional drilling when collecting many types of MNA evaluation data.

D.1.1.5.1 Direct-Push Platforms

Direct-push platforms have gained widespread acceptance in the environmental industry because of their versatility, relatively low cost, and mobility. As opposed to drilling techniques where soil is removed and a borehole is produced, direct-push units use hydraulic pressure or light percussion hammers to advance sampling devices and geotechnical and analytical sensors (see **Table D.2**) into the subsurface (USEPA, 2001c). The two major classes of direct-push platforms are Cone Penetrometer (CPT) and rotary hammer systems. A brief description of each platform is included in the following paragraphs. A comparison of DPT is included in Table D.1.

D.1.1.5.2 Cone Penetrometer

CPT systems are generally the larger of the two direct-push platforms. CPT systems are usually mounted on a 10- to 30-ton truck. A hydraulic ram is used to push the penetrometer tip and push rods into the subsurface, often to depths in excess of 100 feet below ground surface (bgs), depending on soil conditions (USEPA, 2001c).

CPT systems can advance a full range of soil, soil vapor, and ground-water samplers. Piston-type samplers are used to collect relatively undisturbed soil samples without generating soil cuttings. The soil sampler is initially pushed in a closed position to the desired sampling interval, and the inner cone tip of the sampler is retracted about 12 inches, exposing a hollow soil sampler with inner liner. The hollow sampler is pushed in a locked "open" position to collect a soil sample. Once filled, the sampler and push rods are retrieved and brought to the surface for field anlaysis or transfer into appropriate containers in advance of fixed-base laboratory testing.

TABLE D.1
SOIL SAMPLING TECHNIQUES

Soil Sampling Method	Applicable Sampling Depth(s)	Advantages	Limitations/Concerns
Soil Punch/Hand Auger	Surface Shallow	• Easy to operate; requires minimal training. • Sample tubes may be sealed with Teflon® caps for the collection of VOC samples.	• May be very difficult to use in very stiff or gravelly soil.
Scoop or Shovel	Surface Shallow	• Often the only method available when mixed materials are present or as a means of extracting materials during channel sampling.	• Relatively high degree of physical distrubance of samples.
Ring Sampler	Shallow	• Collects samples with constant cross-sectional areas to facilitate data reporting on a per unit area basis.	• Removal of cores is often difficult in very loose sandy soil and in very tight clayey soil.
Soil Probe (hand-operated)	Shallow Medium	• Easy to operate; requires minimal training. • Collects 12 or 18 inches of intact, relatively undisturbed soil core.	• May be very difficult to use in very stiff or gravelly soil. • Long cores taken from tight, clayey soils are hard to extract after the first segment or two.
Trench Sampling with a Backhoe	Shallow Medium	• Appropriate for sampling areas where there is considerable rubble, wood, rock, scrap metal or other obstructions present in the soil.	• OSHA requirements may apply if personnel enter a trench to collect samples (i.e., excavation must be properly sloped or otherwise supported). • Disposal of the excavated material must be considered. Replacing excavated materials could create contaminant migration pathways.

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Soil Sampling Method	Applicable Sampling Depth(s)	Advantages	Limitations/Concerns
Direct Push Techniques (DPT) (See below for a comparison of cone penetrometer [CPT] and rotary hammer DPT)	Shallow Medium	• Collect continuous or discrete cores of unconsolidated materials. • Does not generate cuttings, so there is little or no potentially contaminated soil to dispose. • No drilling fluids or lubricants required. • Sampling and data collection may be faster, reducing the time needed to complete an investigation and increasing the number of sample points that can be collected during the investigation. • In situ emplacement of geophysical and analytical instruments allows the collection of large quantities of information regarding subsurface soils and contaminants in near real time. • Closed sampling systems and on-board analytical instruments allow samples to be analyzed in the field, avoiding laboratory turnaround time, remobilization time, and associated expenses. • Equipment is highly mobile. • Method is relatively inexpensive and requires minimal training to operate compared to traditional drilling.	• Limited to unconsolidated materials. DPT cannot be used to penetrate bedrock layers, concrete footings or foundations, or other high-density barriers. • Presence of soft layers overlying hard layers can alter the alignment of the probe resulting in equipment damage and questionable sample collection depths and locations. • Practical vertical sampling limits are about 100 feet for rotary hammer rigs and 150 feet for CPT rigs. • Well diameter is typically limited to 1.5 inches or less. The resulting small-diameter wells must be sampled using small-diameter samplers or tubing, limiting their usefulness for some applications. Regulatory agency acceptance of small quantities varies by state.

TABLE D.1
SOIL SAMPLING TECHNIQUES (Continued)

Soil Sampling Method	Applicable Sampling Depth(s)	Advantages	Limitations/Concerns
Cone Penetrometer (CPT)	Shallow Medium	• Relatively inexpensive (typical costs for a CPT system with lithologic and sampling tools can vary from $1,000 to $2,000 per day, not including mobilization costs). • Piston-type samplers collect relatively undisturbed soil samples without generating soil cuttings. • Geotechnical sensors used with CPT systems provide a rapid and economical means of determining the soil stratigraphy, relative density, strength as well as hydrogeologic conditions such as the hydraulic conductivity and the static and dynamic pore pressure. • Chemical sensors used with CPT systems provide a rapid and economical means of determining the presence and relative magnitude of fuel contamination in the subsurface.	• CPT units are not equipped to drill through concrete because they have no rotary capability. • Because of the complexity of the analytical methods and the specialized requirements for operating CPTs, CPT operation takes considerable experience. For this reason, most CPTs are designed to be operated by trained technicians. • CPT systems tend to be large, and cannot be used in tight quarters or on sensitive surfaces (e.g., residential lawns) as readily as many of the rotary hammer configurations.
Rotary Hammer DPT	Shallow Medium	• Relatively inexpensive (daily cost for an average-size rotary hammer system, outfitted with samplers and a two-man sampling crew, ranges from $1,000 to $2,000, not including mobilization costs). • Can be installed on numerous size platforms, with varying mobility, therefore are more likely (than a CPT or conventional drill rig) to access areas within tight quarters (e.g., inside buildings) or in sensitive areas (e.g., residential lawns, wetlands).	• Requires less training than CPT; however, it is essential that the operator be familiar with the limitations and operation of the system and have a complete understanding of the sampling tools associated with the system prior to operation. • Percussion advancement precludes use of specialized geophysical measurements (e.g., friction, tip resistance) that are commonly used with CPT rigs.

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TABLE D.1
SOIL SAMPLING TECHNIQUES (Continued)

Soil Sampling Method	Applicable Sampling Depth(s)	Advantages	Limitations/Concerns
Hollow–stem Auger (HSA)	Shallow Medium Deep	• Able to drill in unconsolidated materials and collect relatively undisturbed samples. • Continuous coring of geologic materials is possible using split-barrel or thin-wall samplers. • Lithologic or geologic logging from cuttings or cores. • Drilling fluids are not required. • Drilling is moderately rapid. • Equipment is relatively mobile and widely available. • Relatively inexpensive.	• Drilling is difficult in units that contain very coarse gravel, cobbles, or boulders. • Borehole is limited to depths generally less than 150 feet. • Drilling in non-cohesive, unconsolidated, saturated materials can be difficult due to "running or flowing" sands. • Maximum borehole diameter is about 18 inches.
Direct-rotary Drilling with Water-based Fluid	Medium Deep	• Able to drill in unconsolidated materials, including bouldery till and course stratified deposits, and in consolidated materials (unlimited depth for environmental studies). • Allows coring of unconsolidated and consolidated materials using split-barrel samplers. • Lithologic or geologic logging from cuttings or cores. • Drilling is rapid. • Equipment is widely available.	• Rotary rigs tend to be large and heavy and are therefore limited to areas of stable surface soils. • Drilling fluid or lubricants can alter or contaminate subsurface materials. • Drilling is difficult in geologic materials with large boulders. • Borehole diameter usually is 12 inches or less.
Direct Air-rotary Drilling	Medium Deep	• Able to drill in consolidated, partly consolidated, and unconsolidated geologic units (unlimited depth for environmental studies). • Allows coring of unconsolidated and consolidated materials using split-barrel samplers. • Lithologic or geologic logging from cuttings or cores. • Drilling is rapid. • Equipment is readily available.	• Air rotary drilling rigs tend to be large and very heavy. Thus, they are typically limited to paved or dirt roads or areas where surface stability is sufficient to support the rig weight. • Borehole diameter is 24 inches or less. • Air, foam, or lubricants can contaminate subsurface materials; filters can be used to clean air prior to injection. • Air stream could carry VOCs to the surface, requiring extra safety precautions for drillers. • Cost can be high.

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TABLE D.1
SOIL SAMPLING TECHNIQUES (Concluded)

Soil Sampling Method	Applicable Sampling Depth(s)	Advantages	Limitations/Concerns
Cable-tool Drilling	Medium Deep	• Drilling possible in most types of subsurface conditions including consolidated and unconsolidated materials, cobbles, boulders, and cavernous or fractured rock. • Able to drill to depths of up to 5,000 feet. • Excellent recovery of geologic materials over entire depth of drilling with split-barrel sampler. • Lithologic or geologic logging from cuttings or cores. • Does not require drilling fluids..	• Cable tool rigs tend to be very large and heavy resulting in the need for stable soils capable of supporting the rig weight. • Low penetration rates when drilling fine-grained materials. • Borehole diameter is usually 8 inches or less. • Percussion action could damage physical properties of the hydrogelologic units. • Drilling rates can be slow.
Vibration Drilling (also called Sonic, Rotasonic, or Sonicore Drilling)	Medium Deep	• Drilling possible in unconsolidated and consolidated materials, through boulders, wood, concrete, and other construction debris (unlimited depth for environmental studies). • Can obtain large-diameter, continuous, and representative cores of unconsolidated and consolidated materials. • Drilling fluids usually not required. • Drilling is much more rapid than most methods. • Few cuttings produced, reducing waste disposal.	• Rotosonic rigs tend to be very large and very heavy and typically require the construction of stabilized roads and drilling pads. • Borehole diameter is 12 inches or less. • Drilling and sampling in consolidated materials requires addition of water or air or both to remove cuttings. • Mobilization of a rotosonic rig and all of the support equipment tends to be expensive.

Sources: Modified from USEPA, 1992, 1995a, 2001c; United States Geological Survey (USGS), 1997.

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TABLE D.2
FIELD SCREENING TECHNIQUES FOR SOIL

Field Sampling Method	Description	Advantages	Limitations/Concerns
Qualitative Screening Technologies			
Flame Ionization Detector (FID)	Detects and measures the level of total ionizable organic compounds (including methane) in the ambient air at a well or in a container headspace. The FID has positive or negative response factors for each compound depending on the selected calibration gas standard.	• Equipment is portable and rugged. • Provides real-time results. • Most sensitive to aliphatic hydrocarbons. • Relatively inexpensive to rent or purchase.	• Ambient air temperatures less than 40 degrees Fahrenheit will cause slower responses; relative humidity greater than 95 percent can cause inaccurate and unstable responses. • Interpretation of readings requires training and experience with the instrument. • Does not respond to inorganic substances. • Moderate training required to operate.
Photo Ionization Detector (PID)	Measures ionizable organic vapor levels in the air.	• Equipment is portable and rugged. • Provides real-time results. • Requires less training than FID. • Most sensitive to aromatic hydrocarbons. • Relatively inexpensive to rent or purchase.	• Detects total concentrations and is not generally used to quantify specific substances. • Cannot detect methane or substances with ionization potentials greater than that of the ultraviolet (UV) light source. • Readings can be affected by high wind speeds, humidity, condensation, dust, power lines, and portable radios. • Dust particles and water droplets (humidity) in the sample may collect on the light source and absorb or deflect UV energy, causing erratic responses.
Total Volatile Hydrocarbon Meter	Measures petroleum-related organic vapor levels in the air.	• Equipment is portable and rugged. • Provides real-time results. • Sensitive to volatile hydrocarbons only. Thus very useful as a screening tool at fuel-release sites. • Relatively inexpensive to rent or purchase.	• Detects total volatile hydrocarbons, thus only useful for field screening at fuel-release sites. • Is not sensitive to a wide range of volatile compounds and is thus not generally used for health and safety applications.

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Field Sampling Method	Description	Advantages	Limitations/Concerns
Qualitative Screening Technologies (Concluded)			
Fluorescence Instrumentation (e.g., ultraviolet [UV] light, Fuel Fluorescence Detector [FFD])	A subsurface sample is bombarded with a UV light source (the FFD uses a mercury lamp) that causes petroleum hydrocarbons in the sample to fluoresce. The fluorescence is used to identify and qualitatively measure the contaminant.	• Equipment can be combined with a CPT advancement system, thereby reducing investigation-derived waste, and site characterization time and expense. • FFD provides continuous output fluorescence over the entire depth of the borehole. • Provides real-time data. • More affordable than the similar method of laser induced fluorescence (described below).	• Qualitative data are generated for PAHs. Semi-quantitative data are obtainable for other hydrocarbons (e.g., jet fuel, diesel, unleaded gasoline, home heating and motor oils). • Typical detection limit for TPH in sand is 100 ppm. • Significant training is required.
Semi-Quantitative Screening Technologies			
Colorimetric Test Kits	Self-contained analytical kits that use a chemical reaction that produces color to identify contaminants, both qualitatively and quantitatively.	• Minimal training required; most test kits can be used properly by a novice with some initial supervision. • Colorimetric indicator tubes and reagent kits are available for most common classes of contaminants. • Kits are portable; most require disposable batteries or no power source at all. • Most analyses provide rapid results. • Provide real-time data. • Inexpensive to purchase and operate.	• Minimum sample volume is usually required to perform tests. • Some analyses are subject to interference by other chemicals. • Target analytes must be known prior to selecting test kit. • Results can be affected by soil matrix, naturally occurring organic materials, and water content.
Infrared (IR) Spectroscopy	Portable IR detectors measure the absorbance of IR radiation as it passes through sample extracts.	• Useful for measuring the concentration of total hydrocarbons in the C_6 to C_{26} range. • Equipment is portable. • Provides real-time data.	• Results are biased toward hydrocarbons greater than C_{12} because of their greater response to IR and lower tendency to volatilize during extraction. • Not effective for measuring VOCs and lighter petroleum hydrocarbons. • Results cannot by correlated with health or environmental risks because all hydrocarbons are grouped together and presented as one number. • Method is more expensive than other semi-quantitative screening methods.

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TABLE D.2
FIELD SCREENING TECHNIQUES FOR SOIL (Continued)

Field Sampling Method	Description	Advantages	Limitations/Concerns
Semi-Quantitative Screening Technologies (Continued)			
Fiber Optic Chemical Sensor	Operates by transporting light which, either by wavelength or intensity, provides information about analytes in the environment (air or water) surrounding the sensor.	• Used to measure total volatile petroleum constituents (such as BTEX), SVOCs and chlorinated VOCs such as TCE, PCE, and carbon tetrachloride in water, air, or soil vapor. • Allows for in situ and real-time monitoring even in deep wells. • Instrument is small in size due to small fiber optic diameters.	• Not capable of distinguishing individual compounds. • Detection limits tends to be higher than other quantitative field analytical methods (e.g., gas chromatography). • Some sensors are temperature and time dependent, and may have to be recalibrated after extended use.
Field Gas Chromatograph (GC)	Used for constituent-specific analysis of soil, soil vapor, and ground water samples for volatile and semi-volatile hydrocarbons. Consists of a column and detector (PID or FID).	• Definitive compound identification is possible. • Provides the highest data quality of all commonly used field analytical methods. Comparable to fixed-based laboratory results. • Low detection limits (approximately 2 mg/kg for soil). • Portable GCs may be carried into the field; transportable GCs are mounted to a mobile lab or DPT platform.	• Moderate to significant training is required to operate a field GC. • Extraction efficiency in clays and organic-rich soils may be lower than in other soil types. • Operating temperature range is generally between 40^o and 104^o F. • Certain chemicals may cause interference (e.g., alkanes with BTEX or PAH). • Instrument purchase/rental costs relatively expensive.
Immunoassay Test Kits	Kits use antibodies to identify and measure target constituents through the use of an antibody-antigen reaction.	• Minimal training required. • Available for a wide range of organic and inorganic target analytes (see USEPA, 2001c). • For fuels, well-suited for measuring lighter aromatic petroleum fractions. • Reasonable correlation with laboratory results has been observed. • Equipment is portable and no electricity is required. • Test kits are relatively inexpensive.	• Do not perform well for heavy petroleum hydrocarbons (e.g., motor oil, grease). • Must be used within each manufacturer's specified temperature range (generally between 40^o and 90^o F). • Organic and clay-rich soil may limit effectiveness of extraction. • Prior knowledge of target analytes and potential interferences necessary to select the correct test kit.

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Field Sampling Method	Description	Advantages	Limitations/Concerns
Semi-Quantitative Screening Technologies (Concluded)			
Field Portable X-ray Fluorescence (FPXRF)	Field-portable, handheld device for simultaneously measuring a number of metals in soils and sediment.	• Most instruments weigh less than 30 pounds and can be operated using battery power for 8 to 10 hours. • A sample can be analyzed in less than five minutes. • Little or no sample preparation is needed; samples can be analyzed in situ or, for greater accuracy, by collecting a sample and placing it in a separate sample cup for analysis. • No solvents or acids are used for sample extraction and no waste is generated.	• Detection limits for certain metals are high. • A specific license is required to operate some FPXRF instruments, and there is usually a fee to attend a radiation safety course, obtain the necessary paperwork, and for the operating license. • Concentrations of elements in different types of soil or matrices might change, causing interferences between measured elements.
Direct Push Sensors	Direct push analytical systems incorporate sensors that utilize XRF, laser-induced fluorescence (LIF) or a membrane interface probe (MIP) (see USEPA, 2001b for additional analytical tools) directly into the probe that is advanced with the direct-push tooling into the subsurface.	• Real-time or near real-time data to be generated in the field while sampling, without the many requirements associated with sample management • Generates minimal investigation-derived waste. • Rapid and detailed assessment at a lower overall cost than could be achieve with more traditional methods such as drill rigs and fixed-base laboratories. • LIF attachments can detect gasoline, diesel fuel, jet fuels, fuel oil, motor oil, grease, and coal tar in the subsurface. • MIPs can evaluate subsurface VOC concentrations.	• Detection limits can be higher and precision and accuracy lower than with traditional analytical methods. • Because experienced operators are generally required, it may not be possible to lease the systems; many may be offered as contract services only. • Practical vertical sampling limits are about 100 feet for rotary hammer rigs and 150 feet for CPT rigs. Varies widely with lithology.
Geophysical Technologies			
Borehole Geophysical Logging	Geophysical logs are used to characterize lithology, areas of fractures, and areas of alteration within each borehole. Often combined with DPT.	• Provides a continuous profile of response versus depth. • Data can be correlated between adjacent wells. • Can be used to confirm the locations of water-producing zones in boreholes.	• Borehole logging equipment is relatively expensive and must be transported to the well. • The radius of investigation may be small, and may not be representative of the bulk formation.

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TABLE D.2
FIELD SCREENING TECHNIQUES FOR SOIL (Concluded)

Field Sampling Method	Description	Advantages	Limitations/Concerns
Geophysical Technologies (Concluded)			
Direct Push Electrical Conductivity/ Resistivity	Measurements and logs of soil conductivity supply information about the lithologic features of a site. Changes in conductivity and resistivity may indicate the presence of hydrocarbons.	• Beneficial for site characterization and mapping to support placement of monitoring wells. • Define subsurface geologic and hydrogeologic conditions. • Electrical resistivity may be applicable for the detection of subsurface toluene.	• Experience is needed to calibrate and interpret logs. • Large metal objects can cause interference. • Changes in electrical conductivity due to site conditions may be greater than changes due to the presence of hydrocarbons.
Ground Penetrating Radar (GPR)	GPR uses a transmitter that emits pulses of high-frequency electromagnetic (EM) waves into the subsurface. The EM energy that is returned to the surface provides information about subsurface stratigraphy.	• Measurements are relatively easy to make and are not intrusive. • GPR data can often be interpreted right in the field without data processing. • Graphic displays of GPR data often resemble geologic cross sections.	• Often, the depth of penetration is limited by the presence of mineralogical clays or high conductivity pore fluid. • The accuracy of a GPR survey is dependent upon picking travel times, processing and interpretation, and site-specific limitations.
Magnetometry	Magnetometers measure ambient magnetic fields emanating from terrestrial forces, natural ferrous minerals or ferrous alloys found in cultural objects.	• Widely accepted technology for the location of ferrous masses that are either cultural or natural (e.g., locating buried ferrous drums, tanks, pipes, ordnance, abandoned well casing, boundaries of landfills, mineralized iron ores). • Minimal training required to operate most units. • Equipment is mobile and no electricity is required. • Systems are readily available to rent from vendors.	• Magnetometers are subject to magnetic fields from unwanted ferrous materials (e.g., ferrous fences, vehicles, buildings, ferrous scrap & debris, natural soil minerals, above ground or underground utilities, lightning). • Skilled personnel are required to analyze and interpret results. • Typically will not work inside buildings.

Sources: Modified from USEPA 1995b, 1997a, 1997b, 2001a; Applied Research Associates, Inc., 1999; Advanced Geological Services, 2002; Phillips and Fitterman, 1995; Olhoeft, 1992.

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D.1.1.5.3   Rotary Hammer DPT

A rotary hammer system is usually mounted on a pick-up truck, van, or small tracked vehicle. The Geoprobe® system is an example of a commonly-used rotary hammer system. This platform uses a combined force generated by the static weight of the vehicle on which it is mounted and a percussion hammer to advance steel rods and either a sampler or analytical device.

Four main types of soil samplers are used with rotary hammer systems: discrete, continuous, dual-tube, and hollow-stem auger (HSA). The discrete soil sampler is the most common of the four types. This sampler often uses a piston-activated system that can be pushed to the desired depth and then opened for collection of a sample from a discrete depth interval. Continuous soil sampler systems are very similar to the discrete sampler but do not require piston activation systems. Dual-tube samplers create a casing around the area where soil will be collected with a continuous or discrete soil sampler. The HSA is used only with the most advanced rotary hammer systems that have sufficient torque to advance the auger flights. This system is capable of installing small-diameter monitoring wells or acting as a temporary casing for other direct-push samplers in collapsing soils.

D.1.1.6   Field-Screening Techniques

The most expensive part of an environmental assessment is often laboratory analytical services. To increase the cost-effectiveness of a soil sampling and analysis program, it may be desirable to use field-screening techniques to reduce the number of samples submitted to the laboratory for chemical analysis. According to Hood *et al*. (2002), a field-screening method (for both soil and ground water) should include, at a minimum:

- Speed;
- Adequate sensitivity;
- Selectivity, if appropriate;
- Acceptable levels of relative accuracy and repeatability;
- Appropriateness for the contaminants expected to be encountered at the site;
- Ease of use by "non-chemists";
- Safety features (minimized exposure to dangerous materials such as halogenated solvents, toxic reagents, etc);
- Equipment that is hardened and protected for adverse conditions often encountered in the field;
- Simple to operate; and
- Minimum support services required such as running water, heat, and electricity.

Table D.2 describes several available field-screening techniques for contaminants in soil, and provides information on the types of chemical constituents typically evaluated by each technique. A comparison of typical uses of the data generated by field-screening techniques is

included as **Table D.3**. In addition, selected soil analysis probes that can be used to detect subsurface contamination are described in Section 3.3.3.1.1 of the main text in this document.

D.1.1.7   Sample Collection Protocol

Proper techniques for sample collection and sample preparation are essential components of a representative soil sampling program. Sample collection refers to the number and volume of samples collected. Sample preparation refers to activities that are performed prior to submitting a sample for analysis. This section discusses several important aspects of sample collection and preparation.

How a sample is collected can affect its representativeness. The greater the number of samples collected from a site, and the larger the volume of each sample, the more representative the analytical results will be. The number of samples needed will vary according to the particular sampling approach that is being used. Sample collection strategies are discussed in detail in USEPA (1995a), and are briefly summarized in the following sub-sections.

D.1.1.7.1   Homogenizing

Homogenizing is the mixing or blending of a soil sample, after all aliquots have been combined, in an attempt to provide uniform distribution of contaminants within the homogenized volume. Ideally, homogenization ensures that portions of the containerized samples are equal in composition, and are representative of the total soil sample collected. Manually homogenizing samples is typically done using a stainless steel scoop and a stainless steel bowl, or a disposable scoop and container. Samples may also be homogenized using a mechanically-operated stirring device (USEPA, 1995a). Homogenizing of samples for VOC analysis is not typically performed because the homogenization process is likely to increase volatilization, resulting in loss of VOC contaminants from the soil sample to air.

D.1.1.7.2   Splitting

Splitting samples after collection and field preparation into two or more equivalent parts is performed when two or more portions of the same sample need to be analyzed separately. Split samples are often collected in enforcement actions to compare sample results obtained by a regulatory agency with those obtained by the potentially responsible party. Split samples also provide a measure of sample variability (USEPA, 1995a). Splitting soil samples should take place after the sample has been homogenized. Splitting is usually accomplished by carefully filling two or more sample jars simultaneously with alternating spoonfuls of a homogenized sample.

D.1.1.7.3   Compositing

Compositing is the process of physically combining and homogenizing several individual soil aliquots. Composite samples provide an average concentration of contaminants over a certain number of sampling points, which reduces both the number of required lab analyses and the sample variability. Similar to homogenization (Section D.1.1.7.1), compositing is not typically performed when samples are being collected for volatile compound analysis because volatilization may occur in the compositing process. Compositing requires that each discrete

TABLE D.3
TYPICAL USES OF DATA GENERATED BY FIELD ANALYTICAL
AND SITE CHARACTERIZATION TECHNOLOGIES

Technology	Contaminant Screening	Site Characterization	Cleanup Monitoring	Compliance Monitoring	Confirmation Sampling	Health & Safety Monitoring	Waste Characterization	Risk Assessment
Flame Ionization Detector (FID)	✓					✓		
Photo Ionization Detector (PID)	✓					✓		
Total Volatile Hydrocarbons (TVH) Meter	✓							
Fluorescence Instrumentation	✓	✓						
Colorimetric Test Kits	✓	✓	✓	✓			✓	
Infrared (IR) Spectroscopy	✓	✓	✓	✓				
Fiber Optic Chemical Sensor	✓	✓						
Field Gas Chromatograph (GC)	✓	✓	✓	✓	✓	✓		
Immunoassay Test Kits	✓	✓	✓	✓	✓		✓	
Field Portable X-ray Fluorescence (FPXRF)	✓	✓	✓	✓	✓			✓
Direct Push Sensors	✓	✓						
Borehole Geophysical Logging		✓						
Direct Push Electrical Conductivity/Resistivity	✓	✓						
Ground Penetrating Radar	✓	✓						
Magnetometry		✓						
Soil vapor Surveys	✓	✓	✓					

Sources: Modified from USEPA 1995a, 1997a, 1997b, 2001a, Applied Research Associates, Inc., 1999; Advanced Geological Services, 2002.

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aliquot be the same volume or weight, and that the aliquots be thoroughly homogenized (USEPA, 1995a).

D.1.1.7.4   Sample Containers and Preservation

Soil samples can be placed in clean, analyte-appropriate jars and transported to the analytical laboratory. For samples to be analyzed for VOCs however, this approach, which incorporates a relatively large amount of open-air handling and disturbance of soils, may promote loss of volatiles. Alternately, samples may be collected directly into liners or sleeves inserted into the sampling device. These liners, which may be constructed of various materials (e.g., brass, stainless steel, acetate, polyvinyl chloride [PVC], polyethylene), can be capped and shipped directly to the laboratory. Use of liners minimizes sample disturbance and loss of VOCs. When field sample preservation is required per USEPA Method SW5035, EnCore® samplers can be used (e.g., ASTM, 1999). This is a proprietary device that allows the sampler to collect and transport samples to the laboratory within 48 hours, without preserving them in the field. Alternately, Method SW5035 requires field preservation of soil samples with methanol or sodium bisulfate. Prior to mobilization to the field, applicable federal or state guidance or regulations regarding the appropriate soil sample collection and containerization techniques for a particular site should be reviewed and incorporated into the soil sampling program.

D.1.2   Soil Vapor Sampling

Soil vapor sampling involves the collection of vapors occupying the pore spaces of soils. Soil vapors are composed of air, water vapor, naturally occurring and/or anthropogenic organic compounds, organic compounds migrating from deep fossil fuel reserves, and any other constituents capable of partitioning from liquid and solid materials into the vapor phase under ambient conditions. Soil vapor samples are collected and analyzed to determine the composition and spatial distribution of the selected analytes. The results may be interpreted in terms of soil moisture content, environmental contamination, fossil fuel presence, or occurrence of biological endproducts, depending on the application and questions of interest or concern. Soil vapor surveying is an effective, efficient, and relatively non-disruptive method of delineating the nature and spatial extent of contaminants containing volatile and semi-volatile organic compounds (including many petroleum fuels). Soil vapor sampling programs are designed to focus subsequent sampling investigations on contaminated areas (W.L. Gore & Associates, 2003).

Two general methods of soil vapor sampling exist - active and passive. Both soil vapor sampling methods are effective tools in understanding the subsurface composition of soil vapors, and both methods have advantages and disadvantages. An advantage of active soil vapor methods is that this technique can provide near-real-time data on VOCs at a site suspected of having subsurface contamination. Advantages of passive soil vapor sampling are that this technique 1) can be used to collect soil vapor from low-permeability and high-moisture settings and 2) is capable of detecting and reporting semi-volatile organic compounds and compounds present at very low concentrations (e.g., hydrocarbon vapors migrating to the surface from deep petroleum reserves) (W.L. Gore & Associates, 2003). The following text provides an additional description of active and passive soil vapor sampling techniques.

D.1.2.1   Active Soil vapor Sampling

Conventional or active approaches involve inserting a hollow-stemmed probe into the subsurface and "actively" removing a sample of soil vapor from the pore spaces. This sample is typically transferred to a container for later analysis, or analyzed at the site using field analytical equipment. For this technique, a thin stainless steel probe is inserted into a hole made in the soil or is itself driven into the soil, typically to a depth of at least two feet bgs. The deeper the sampling depth, the less chance for short-circuiting of surface air along the probe rods and into the sample, and the less chance for getting false negatives due to volatilization of near-surface contaminants to the atmosphere. The hole is sealed around the probe and a sampling pump is attached. Samples are then collected in Tedlar® bags, sorbent cartridges, or SUMMA® canisters. The samples are analyzed using an flame ionization detector (FID), photoionization detector (PID), or other appropriate gas chromatography (GC) technique. It is important to note that the ability of the soil vapor technique to detect contaminants diminishes the further it is from the source because contaminant concentrations in soil are diminished (USEPA, 1995a). A common method for collecting active soil vapor samples is the use of a direct push platform. Active soil vapor samples are typically analyzed for VOCs.

D.1.2.2   Passive Soil vapor Sampling

With passive soil vapor sampling, collectors containing adsorbent materials are placed in the subsurface and left for a period of time. Organic vapors, migrating through the subsurface, encounter the collector and are "passively" collected onto the adsorbent material. The collectors are retrieved and analyzed following the field survey.

One such device used in passive soil vapor sampling is the GORE-SORBER® Module. The module is constructed entirely of GORE-TEX® membrane. This membrane is an expanded polytetrafluorethylene (ePTFE) which is chemically inert, microporous (vapor permeable), and hydrophobic. Pore spaces are designed to be orders of magnitude smaller than a liquid drop of water. Organic vapors present in the soil migrate unimpeded through the membrane to the adsorbent material contained in the GORE-SORBER®. The module itself is approximately 1 foot in length and contains enough sorbers for two samples. This allows for duplicate analysis if required. Each module is stored in individual containers and is uniquely numbered and tracked throughout the project (W.L. Gore & Associates, 2003).

Advantages of passive soil vapor sampling using a device such as the GORE-SORBER® module include increased detection sensitivity and greater flexibility of use in a variety of environmental conditions. Disadvantages include the lack of real-time data to guide placement of subsequent samples.

D.1.3   LNAPL Characterization Methodologies

D.1.3.1   LNAPL Occurrence in the Subsurface

LNAPLs are relatively water-insoluble organic liquids (e.g., gasoline, diesel) that are less dense than water and typically spread on top of the capillary fringe and water table (Karklins, 1996). LNAPLs may exist as continuous, free-phase liquids (mobile LNAPL) and/or as liquids

trapped above and below the water table (residual LNAPL). As described in Appendix C, residual LNAPL (commonly referred to as "soil contamination") includes contaminants that are sorbed to soil particles or present as droplets trapped between soil particles (i.e., occluded). Accurate site characterization may be technically challenging due to the heterogeneity of subsurface media and variability of subsurface conditions. It is not uncommon to observe a "patchy" distribution of LNAPL over a relatively small area at a site, or the transient presence of LNAPL in a well (Newell *et al.*, 1995).

D.1.3.2   Defining Objectives

Specific objectives of an LNAPL sampling program typically include identification and delineation of:

- Mobile and residual LNAPL;

- Migration rates/directions of the mobile phases and geologic controls on LNAPL movement; and

- LNAPL physical properties (e.g., density, viscosity, and chemical composition).

The level of detail and the type of data required will be site-specific, and may be partially dictated by the remedial technologies under consideration and economic constraints (USEPA, 1995a).

D.1.3.3   Mobile LNAPL Characterization

Recovery potential for mobile LNAPL is controlled by such factors as LNAPL viscosity, density, and relative permeability (Testa and Packowski, 1989). For example, high LNAPL viscosity, high residual water saturation, and low permeability will tend to reduce LNAPL recovery rates. Monitoring wells, borings, and test pits installed in areas of potential LNAPL releases are some of the key methods for characterizing mobile LNAPL.

Monitoring wells at fuel-release sites that may contain mobile LNAPL should generally be screened across the water table to enable detection of mobile LNAPL, if it is present, and to enable collection of both ground water and mobile LNAPL samples during periods of varying ground-water elevations. The use of appropriate construction materials should also be considered in monitoring well design. LNAPLs (e.g., jet fuel, kerosene, gasoline) can affect materials used in well construction, sampling, and remediation in two ways. First, the structural integrity of a material may be compromised by corrosion or solvation. Second, dissolved ground-water contaminants from LNAPLs can sorb onto or leach into monitoring materials, affecting ground-water quality measurements (McCaulou *et al.*, 1995). In most circumstances, installation of monitoring wells constructed of PVC should be adequate. Research regarding construction materials specifically designed for LNAPL monitoring is limited; however, recent studies of filter packs for LNAPL recovery wells indicated LNAPL recovery rates were increased using packs with a grain size approximately half of conventional recommendations for recovery wells (Newell *et al.*, 1995).

Determination of physical and chemical properties of LNAPL obtained from wells or separated from soil samples is often required to evaluate many aspects of LNAPL site

<div align="center">D-20</div>

characterization and remedial design. For example, information concerning physical properties such as density and viscosity may be used to assess LNAPL mobility and distribution. It may also be necessary to determine the chemical composition of the LNAPL, which may be used to compute the effective solubility of LNAPL components, estimate how long the LNAPL will constitute a secondary source of contaminants to ground water and soil vapor, and aid in evaluating the applicability of certain remedial technologies such as soil vapor extraction (Newell *et al.*, 1995).

Mobile LNAPL samples can be collected using bailers or, if the LNAPL layer is sufficiently shallow, a peristaltic pump. Ideally, the LNAPL in the well casing should be purged prior to sample collection to allow fresh LNAPL to flow into the well. However, this may not readily occur at some sites, including those with low-permeability aquifer matrix materials. In addition, the LNAPL in the well may be "trapped" above the top of the well screen due to an increase in the ground-water elevation. For these reasons, it is advisable to collect a LNAPL sample prior to purging in the event that fresh LNAPL does not readily enter the well within the required time frame.

D.2   GROUND-WATER CHARACTERIZATION METHODOLOGIES

D.2.1   Elements of a Ground-water Sampling Program

The following elements should be considered in the design of a ground-water sampling program (Barcelona *et al.*, 1985):

- Hydrogeologic setting and desirable sampling frequency;

- Information needs and analyte selection;

- Well placement and construction;

- Well development, hydraulic performance, and purging strategy;

- Sampling mechanisms and materials; and

- Sample collection protocol.

D.2.1.1   Defining Objectives

Before monitoring, it is critical to identify and understand the purpose for monitoring and how the resultant data will be used (Karklins, 1996). Sampling objectives for ground water may include the following (from USEPA, 1995b):

- Identify the presence of contamination, including source, composition, and characteristics;

- Determine if the ground water constitutes a hazardous material for disposal purposes;

- Establish the existence of an imminent or substantial threat to public health and welfare or to the environment;

- Establish the existence of a potential future threat requiring long-term actions;

- Develop containment and control strategies; and

- Evaluate treatment options.

D.2.1.2 Quality Control

The ground-water sampling design should utilize approved standard operating procedures (SOPs) and previously approved sampling designs to ensure uniformity and comparability between sample results. The actual sample collection process should be determined prior to sampling. The sampling design also should be designed to fulfill DQOs. QA objectives should be built into the sampling design, including all necessary QA/QC samples (see Section D.3). Common design errors for ground-water sampling plans include inappropriate 1) well location selection, 2) well construction and development, 3) background sample location selection, and 4) equipment (USEPA, 1995b).

D.2.2 Monitoring Well Design and Placement

Cost-effective positioning of monitoring wells at a particular site requires detailed hydrogeologic information regarding ground-water flow direction, ground-water flow rates, contaminant concentration distribution, and location(s) of potentially sensitive receptors in the vicinity of and/or downgradient from the contaminant plume. Well installation programs are typically iterative programs in that new monitoring well locations are chosen based on data obtained from previously installed monitoring wells or previous ground-water grab samples (e.g., temporary wells or discrete DPT samples), as well as any historic information that may be available. The end goals of any monitoring well installation program should include the following elements at a minimum:

- Definition of ground-water flow direction and rate;

- Delineation of the nature, magnitude, and extent of dissolved contaminant plumes;

- An accurate estimate of the migration rate of the identified plumes;

- Installation of monitoring wells downgradient of the toe of each identified plume to monitor plume migration; and

- Installation of monitoring wells upgradient of potential receptors (i.e., ground-water production wells) to monitor for impact to those receptors.

As described by Wiedemeier and Haas (2002), wells installed for a natural attenuation evaluation should ideally be located in the contaminant source area, along the longitudinal axis of the dissolved plume downgradient from the source area, upgradient and cross-gradient from the plume, and downgradient from the plume (see Section 5.3.1).

The construction of monitoring wells should be accomplished in a manner that minimizes the disturbance of the materials in which the well is constructed. Decontamination of all equipment used for drilling and well installation between borings should play a prominent role in any well installation program to ensure that cross-contamination between borings is avoided. The drill rig and any other pieces of machinery used on site should be checked for fluid leaks prior to the initiation of drilling in an effort to prevent the introduction of new contamination to the site of interest. These preliminary precautions are essential to ensure that artifacts of the drilling process are not detected later in the program and considered to be the result of actual conditions

at the monitored facility (Barcelona *et al.*, 1985). AFCEE (1997) provides an example field sampling work plan that is a useful template for creating a site-specific work plan to describe procedures for monitoring well design, construction, installation, and development.

D.2.2.1 Drilling and Well Completion Methods

The selection of drilling and well completion methods for monitoring well installations should be based on the type of geologic materials to be penetrated, the anticipated depth of drilling, the availability of drilling equipment and supplies, and the potential adverse chemical effects of the drilling and well construction procedures on the samples produced from the monitoring well. The selection of an appropriate drilling method for constructing monitoring wells should be based on minimizing both the disturbance of the geologic materials penetrated and the introduction of drilling air or fluids to the subsurface (Barcelona *et al.*, 1985). **Table D.4** describes several drilling techniques that can be used for monitoring well installation.

D.2.2.2 Monitoring Well Design

Proper installation of monitoring wells requires knowledge of current practices for well installation, both to avoid potential contamination of the well caused by the well construction process itself, and to permit easy access to the subsurface for ground-water sampling and water-level measurement (Nielsen, 1991). Site-specific conditions, in addition to monitoring program objectives, should be considered when determining both the depth and diameter of a monitoring well, as well as screen length and placement. Equally important is the determination of appropriate well construction materials (i.e., well casing, screen material, filter pack, annular seals, and type of surface completion) for the site. A successful monitoring well design should include a review of site-specific conditions such as:

- Purpose or objective of the monitoring program;
- Surficial conditions (e.g., topography, drainage, climate, access);
- Known or anticipated hydrogeologic setting (e.g., geology, aquifer type and physical characteristics, recharge conditions, ground-water/surface water interactions);
- Characteristics of known or anticipated contaminants (e.g., chemistry, density, viscosity, reactivity, potential concentration);
- Anthropogenic influences; and
- Any applicable regulatory requirements (Nielsen, 1991).

The design of a monitoring well should be based on using a suitable drilling technique for the materials anticipated to be encountered, rather than on the most readily available types of drilling equipment or on the equipment used by a preferred driller in the area where the project is located. It is also recommended that cost considerations not be allowed to compromise the collection of valid data needed to meet the goals of the sampling program, as the overall cost to the project by not collecting data necessary to implement a site remediation strategy and achieve site closure will likely far outweigh installation and sampling of a few additional monitoring wells (Barcelona *et al.*, 1985).

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TABLE D.4
WELL DRILLING TECHNIQUES

Drilling Method	Appropriate Sampling Depth(s)	Advantages	Limitations/Concerns
Direct Push Techniques (DPT)	Shallow Medium	• Installation of small-diameter wells or piezometers to screen for water-quality and hydrologic properties. • Well-development and purging efforts can be relatively rapid. • Well screens can be emplaced without exposure to overlying materials. • No drilling fluids or lubricants required. • Installation rate is rapid. • Equipment is highly mobile. • Method is relatively inexpensive and requires minimal training to operate compared to traditional drilling.	• Limited to unconsolidated materials. DPT cannot be used to penetrate bedrock layers, concrete footings or foundations, or other high-density barriers. • Presence of soft layers overlying hard layers can alter in the alignment of the probe and can bend, break, or refuse the rod. • Practical vertical sampling limits are about 100 feet for rotary hammer rigs and 150 feet for CPT rigs. • Well diameter is usually 2 inches or less. • Well screen can become clogged during driving if using an unprotected well screen.
Hollow-stem Auger (HSA)	Shallow Medium Deep	• Able to drill in unconsolidated materials. • Hollow-stem auger acts as a casing and facilitates installation of well casing. • Drilling fluids are not required; use of lubricants can be avoided. • Drilling is moderately rapid in many unconsolidated materials. • Equipment is relatively mobile and widely available. • Relatively inexpensive.	• Drilling is difficult in units that contain very coarse gravel, cobbles, or boulders, or in very dry, fine materials. • Borehole depth generally limited to depths less than 150 feet. • Maximum borehole diameter is about 18 inches.
Solid-stem Auger	Medium Deep	• Able to drill in unconsolidated materials, and weathered and soft-rock units. • Drilling fluids are not required; use of lubricants can be avoided. • Equipment is relatively mobile and widely available. • Relatively inexpensive.	• Presence of cobbles or boulders can result in "auger refusal." Drilling is difficult in very dry, fine materials. • Under saturated conditions, a borehole will usually collapse upon auger removal making casing advancement, and filter pack and annular seal placement, difficult or impossible. • Borehole is limited to depths generally less than 150 feet.

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Drilling Method	Appropriate Sampling Depth(s)	Advantages	Limitations/Concerns
Cable Tool	Medium Deep	• Drilling possible in most types of subsurface conditions including consolidated and unconsolidated materials, cobbles, boulders, and cavernous or fractured rock. • Able to drill to depths of up to 5,000 feet. • Advancement of temporary casing maintains borehole stability and reduces cross contamination. • Allows for easy installation and precise placement of casing. • Well development is relatively easy. • Does not require drilling fluids.	• Low penetration rates when drilling fine-grained materials. • Borehole diameter is usually 8 inches or less. • Percussion action could alter physical properties of geologic units penetrated. • Drilling rates can be slow.
Air Rotary	Medium Deep	• Able to drill in partly consolidated and consolidated geologic units (unlimited depth for environmental studies). • Can estimate yields of water-bearing zones and location of water table. • Casing advancement can be used. • Annulus formed between well casing and borehole wall often can be filter packed and sealed readily. • Drilling is rapid. • Equipment is generally readily available.	• Cannot be used for unconsolidated aquifers; this method relies on the stability and cohesiveness of subsurface materials. • Borehole diameter is 24 inches or less. • Air, foam, or lubricants can contaminate subsurface materials, although filters can be used to clean air prior to injection. • Air stream could carry VOCs to the surface, requiring extra safety precautions for drillers. • Cost can be high.
Power Bucket Auger	Medium Deep	• Able to drill in unconsolidated materials, and weathered and soft-rock units. • Accurate estimate of depth to water table. • Installation of multiple sensors or multiple monitoring wells in a single borehole. • Drilling fluids are usually not required. • Equipment is mobile. • Drilling is moderately rapid. • Relatively inexpensive.	• Drilling is confined to unconsolidated or partly consolidated materials without boulders. • Borehole is limited to depths generally less than 150 feet. • Maximum borehole diameter is about 4 feet. • Casing cannot be advanced. • Cross contamination of ground water along borehole wall can occur. • Borehole collapse can occur during augering. • Heavy equipment required.

TABLE D.4
WELL DRILLING TECHNIQUES (Concluded)

Drilling Method	Appropriate Sampling Depth(s)	Advantages	Limitations/Concerns
Vibration Drilling (also called Sonic, Rotasonic, or Sonicore Drilling)	Medium Deep	• Drilling possible in unconsolidated and consolidated materials, through boulders, wood, concrete, and other construction debris. • Casing is advanced. • Drilling fluids usually not required. • Drilling is more rapid than most methods. • Few cuttings produced, reducing waste disposal. • Equipment is highly mobile, allowing good site accessibility.	• Limited to 500-foot depth. • Borehole diameter is 12 inches or less. • Drilling and sampling in consolidated materials requires addition of water or air or both to remove cuttings.

Sources: USGS, 1997.

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Given that dissolved fuel contaminants are less dense than water, they are typically most concentrated in the uppermost portion of the water-bearing zone (i.e., near the water table). Therefore, well screens should not extend more than 8 to 10 feet into the water-bearing zone. Typically, 10-foot well screens are used that extend from between 2 to 4 feet above to 6 to 8 feet below the water table. This screen placement (relative to the water table) permits detection and sampling of any free product floating on the water table and allows for seasonal ground-water fluctuations. The expected magnitude of temporal water-table fluctuations should be assessed where possible to optimize placement of the screen. If the vertical variation in dissolved contaminant concentrations is not known, then deeper ground water (i.e., greater than 8 to 10 feet below the water table) can be sampled by installing a paired well screened at a deeper depth, or collecting ground-water grab samples at depth using a discrete sampling device such as a HydroPunch® or Ground Water Profiler®, or by the installation of passive diffusion bag samplers (PDBSs) at multiple depths along the well screen (Tunks *et al.*, 2000; Vroblesky, 2001). If contamination is detected in deeper samples using a grab sample or PDBS method, permanent monitoring wells should be installed in an appropriate location, with well screens at the depth(s) of deeper contamination to monitor contaminant concentration.

D.2.2.3 Well Development Techniques

Once a well is completed, it must be prepared for ground-water sampling and water-level measurement by way of well development. The goal of monitoring well development is to remove fine-grained material (e.g., silt, clay, fine sand) and drilling fluid residue from the filter pack and the natural formation in the vicinity of the screened interval of the well. A monitoring well should be developed to allow for the collection of a turbidity-free (to the extent practical), representative ground-water sample for chemical analysis. Four possible methods for monitoring well development are described in **Table D.5**.

D.2.3 Ground-water Sampling

The following subsections provide brief descriptions of recommended procedures and processes for ground-water sampling. AFCEE (1997) provides an example field sampling work plan that is a useful template for developing site-specific work plans for ground-water sampling programs.

D.2.3.1 Sampling Mechanisms and Materials

The selection of appropriate ground-water sampling equipment is based on sampling objectives, the analytical parameters of interest, the type of well being sampled, and other site-specific conditions (USEPA, 1995b). **Table D.6** presents details on various types of ground-water sampling equipment.

D.2.3.2 Sample Collection Protocol

A well-conceived ground-water sampling protocol consists of a written description of the actual sampling and analytical procedures involved in obtaining representative ground-water data. To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol as performed in the field is essential. In addition to noting reference

TABLE D.5
WELL DEVELOPMENT METHODS

Sampling Equipment	Description	Advantages	Limitations/Concerns
Surging/Pumping with Compressed Air	Air is injected directly into the water column and diverted through the well screen to loosen the fines, and results in air, water and fines being forced up the well casing and out of the well.	• Will work for most monitoring wells, regardless of depth to water.	• Air from the compressor must be filtered in order to keep oil from the air compressor from being introduced into the well. • Potentially hazardous vapors and materials may be forced out of the well in an uncontrolled fashion.
Pumping or Overpumping, with Backwashing	Repetitive cycles of pumping or overpumping and backwashing. Backwashing occurs when the pump is shut off and the water in the pump line falls back into the well.	• Pumping forces water and fine-grained material to flow out of the aquifer and into the well. • Backwashing helps prevent bridging of fine-grained material in the filter pack around the well and cleans the well screen.	• Backwashing can potentially affect ground-water chemistry.
Mechanical Surging	A surge block is pulled up through the water column, with the upward movement inducing water to flow from the aquifer back into the well.	• Loosens and removes fine-grained materials from the aquifer adjacent to the screen. • Minimizes the stress to the aquifer by uniformly distributing the force applied over the open interval of the well. • No air or foreign water is introduced into the well.	• Loose materials must subsequently be removed from the well with a bailer or pump. • Vigorous surging could collapse the well casing or screen. • Excessive amounts of loose material could prevent extraction of the surge block.
Bailing	Water is removed by repeatedly lowering and raising a bailer in and out of the well.	• Useful for wells completed in very low-yield formations. • Loosens and removes fine-grained material from the aquifer adjacent to the screen, and removes sediment suspended in the well itself. • No air or foreign water is introduced into the well.	• Relatively slow, especially if bailing is done manually in deeper wells, without the use of a hoist or reel.

Sources: Nielsen, 1999; Barcelona *et al*., 1999; USGS, 1997.

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TABLE D.6
GROUND-WATER SAMPLING EQUIPMENT

Sampling Equipment	Description	Advantages	Limitations/Concerns
Bailer	Hollow rigid tube that fills from the bottom up as it is lowered into the water column.	• Can be constructed of a variety of materials. • Relatively inexpensive to purchase or construct. • Simple to operate and durable. • Nor depth or well diameter limitations. • Light, portable, and easy to decontaminate in the field. • Requires no power source.	• Potential exists to lose VOCs or alter redox-sensitive parameters. • Sample quality highly depends on the skill and care of the operator. • Time consuming and labor intensive, especially for deep wells and wells requiring many well volumes to be purged. • Check valve ball may leak when collecting silt- or sand-laden samples.
Syringe Sampler	A syringe sampler is lowered into the water column, and a plunger or piston is pulled up either mechanically or pneumatically, allowing water to enter the lower sample chamber.	• Can be constructed of a variety of materials. • Relatively inexpensive to purchase or construct. • Requires minimal operator training. • Most have no depth limitations. • Effective at collecting depth-discrete samples. • Light, portable, and usually easy to decontaminate in the field. • Requires no power source.	• Plungers may be prone to bind and leak, especially when collecting silt-laden samples. • Operation may be difficult if the device is lowered into a deep well. • Plungers are typically made of non-inert materials (rubber) unsuitable for VOCs. • Sample transfer can be difficult. • Syringe chambers may have limited sample volume.
Peristaltic Pump	Operate by spinning or rotating an impeller that causes water to be accelerated outward and then upward into the pump's discharge line. The pump is a portable unit that is used in conjunction with flexible tubing.	• Allows for easy, direct in-line filtration of samples. • Portable, easy to use and little operator training is required. • Readily available and relatively inexpensive. • Variable flow rates are possible. • Sample does not contact pump parts. • Can be used in wells of any diameter.	• Requires a power source. • Vacuum may cause volatilization and degassing in gas-sensitive and volatile samples. • Lift restriction of 25 feet or less. • Flexible sample tubing may leach plasticizers and adsorb/desorb VOCs. • Field repair may be difficult.

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TABLE D.6
GROUND WATER SAMPLING EQUIPMENT (Concluded)

Sampling Equipment	Description	Advantages	Limitations/Concerns
Submersible Centrifugal Pump	Operates by spinning or rotating an impeller that causes water to be accelerated outward and then upward into the pump's discharge line. The pump is usually suspended in a monitoring well by its water discharge line or a support cable.	• Collect high-quality and low-turbidity samples at low flow rates. • Capable of variable flow rates. • Moderate to high lift capacity, approximately 300 feet. • Allows for easy, direct in-line filtration of samples. • Can be constructed of relatively inert materials. • Can be dedicated to stick up or flush mount wells.	• Models not capable of low-flow rates are not suited for collecting VOC samples. • Requires external power source – portable systems may require a generator. • Purging and sampling from deep wells may be slow. • Relatively time-consuming to disassemble and decontaminate.
Bladder Pump	A bladder pump consists of a flexible, squeezable bladder encased in a rigid outer casing.	• Collect high-quality and low-turbidity samples at low flow rates. • Sample does not contact mechanical pump parts. • Capable of variable flow rates. • Allows for easy, direct in-line filtration of samples. • Very high lift capacity (up to 1,000 feet). • May be portable or dedicated. • Easily repaired in the field.	• Portable but may be bulky and difficult to transport long distances or over rugged terrain. • Requires compression gas and controller box. • Purging and sampling from deep wells may be slow. • May be time consuming to disassemble and decontaminate. • Bladder may rupture when used in deep wells. • Portable systems may freeze in winter.
Passive Diffusion Bag Sampler (PDBS)	Consists of a low-density polyethylene, lay-flat tube closed at both ends and filled with deionized water prior to deployment. Over time, VOCs in the ground water diffuse across the capsule membrane, and contaminant concentrations in the water inside the sampler attain equilibrium with the ambient ground water.	• Minimized wastewater disposal. • Inexpensive and disposable. • Minimum amount of field equipment is necessary • Low mobilization and equipment costs. • No pumps and hoses to decontaminate. • Minimal training required to be proficient with samplers; easy to deploy and recover. • Multiple samplers can delineate vertical distribution of contamination and aquifer characteristics. • Samples do not contain sediment due to the small pore size of the PDBS material.	• Significant vertical flow in the well may cause VOC concentrations in the PDBS to differ from actual VOC concentrations in the aquifer at the deployment depth. • VOC concentrations represent a period of 48-166 hours; cannot give concentration at a specific time. • Not representative of concentrations above or below the deployment depth; immediate vicinity only. • Not applicable for all VOCs (e.g., MTBE, acetone, styrene, 4-methyl-2-pentanone, SVOCs). • Cannot be used in wells where well screens or filter packs are less permeable than surrounding aquifer.

Sources: Karklins, 1996; AFCEE, 2002

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information (e.g., persons conducting the sampling, equipment used, weather conditions, documentation of adherence to the designated sampling protocol, unusual observations, well name, and well condition), three basic elements of the sampling protocol should be recorded:

- Water-level measurements prior to sampling;

- The volume and rate at which water is removed from the well prior to sample collection (well purging); and

- The actual sample collection, including measurement of well-purging parameters, sample preservation, sample handling, and chain-of-custody (Barcelona *et al*., 1985).

D.2.3.3   Selection of Ground-Water Sampling Locations

Unlike soil sample collection, where several approaches (e.g., judgmental, random, grid) are used to obtain data, ground-water sampling is generally limited to a judgmental sampling approach. Judgmental sampling is the biased selection of sampling locations based on historical information, visual inspection, sampling objectives, and professional judgment. This approach is best used when knowledge exists of the suspected contaminants at the site. Criteria for selecting sampling locations are dependent on the particular site and level of contamination expected. Due to the cost of installing monitoring wells, a judgmental approach is often the most cost-effective; a random, systematic grid, or systematic random approach could result in too many wells that miss the contaminant plume. Although the latter approaches are not often used for ground-water sampling, they may be useful for designing soil vapor testing well installation programs that can be performed in advance of monitoring to assist in the siting of new monitoring wells.

D.2.3.4   Ground-Water Sample Collection

As described in Section 3.4.3.3, MNA-related ground-water sampling at fuel-release sites can be performed using either a low-flow (i.e., "micropurge") method or a well-volume method (i.e., removal of a pre-determined amount of water such as a minimum of three casing volumes). Accurate measurement of redox-sensitive parameters during well purging will be facilitated by a low purge rate and minimal disturbance of the sample (USEPA, 1996).

The low-flow method involves pumping in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates between 0.1 and 0.5 liters per minute are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates of up to 1 liter per minute (USEPA, 1996). Advantages of the low-flow method include minimization of purge-water volumes and sample turbidity, and minimal disturbance of the sampling point thereby maximizing sample representativeness. Potential disadvantages include the potential for lower reproducibility of the sampling results unless the position of the sampling pump intake does not vary between sampling rounds, and collection of the sample from a relatively small volume of the aquifer, which has the potential to be less representative of the average analyte concentration within the screened interval of the well. If the well-volume approach is used, the well-purging rate should not be great enough to produce excessive turbulence in the well. The pump rate during sampling should produce a smooth, constant (laminar) flow rate, and should not produce turbulence during the filling of

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bottles. As a result, the expected flow rate for most wells will be less than 1.0 gallons per minute (gpm; 3.8 liters per minute) in a 2-inch-diameter well, with typical flow rates of about 0.25 gpm (0.95 liters per minute) (USEPA, 2002).

As described in USEPA (1996), bailers and inertial 'foot-valve' type samplers cause uncontrolled and unacceptable levels of sample disturbance for low-flow sampling purposes, and should not be used when redox-sensitive parameters are being measured. However, if redox-sensitive parameters are not part of the data requirements for a particular sampling event, use of bailers, foot-valve pumps, or passive diffusion bag samplers may provide a cost-effective means for monitoring VOC concentrations. USEPA (2002) provides guidance on both the low-flow and well-volume ground-water sampling methodologies.

D.2.3.5   Filtration Procedures

It may be necessary to filter ground-water samples during field collection. Reasons for filtration of ground-water samples include: 1) removal of suspended solids to analyze the dissolved fraction of a chemical compound, 2) determining the percent of suspended solids in a sample, 3) performing a separate analysis of constituents attached or sorbed to suspended solids, and 4) performing field analysis for inorganic chemical constituents.

At a fuel-release site, filtration will generally be performed when analysis for dissolved lead is desired. When sampling using a pump, filtration can be performed using an in-line filtration device consisting of a holder/filter system, typically in cartridge form, in which inlet and outlet connections can be made to enable pressure filtration. The filter cartridge is connected directly to the discharge tubing of the ground-water sampling device. Otherwise, vacuum or pressure filtration devices must be used. Both vacuum filtration and pressure filtration involve transfer of the sample water from a sample collection device or other container, through a porous filter, and into the field filtration device. In vacuum filtration, the sample is pulled through the filter, while in pressure filtration, the sample is pushed through the filter using compressed air as the driving force. A 0.45-micron filter size is typically used. Note that, for VOCs, use of low-flow sampling techniques (rather than filtering) is the preferred method for addressing turbidity in ground-water samples.

D.2.3.6   Field Screening and Water Quality Measurements

In addition to reducing analytical costs, field analytical screening for ground water is used as a tool for siting monitoring wells and for on-site health and safety assessment during well drilling activities. Section D.1.1.6 describes several considerations for choosing an appropriate field-screening technique. **Table D.7** describes several available field-screening techniques for ground water, and provides information on the types of parameters and chemical constituents typically evaluated by each technique.

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TABLE D.7
FIELD SCREENING TECHNIQUES FOR GROUND WATER

Field Screening Technique	Description	Advantages	Limitations/Concerns
Colorimetric Test Kits	Self-contained analytical kits that use a chemical reaction that produces color to identify contaminants, both qualitatively and quantitatively.	• Minimal training required; most test kits can be used properly by a beginner with some initial supervision. • Colorimetric indicator tubes and reagent kits are available for most common classes of contaminants. • Kits are portable and most use disposable batteries or require no power source at all. • Most analyses provide rapid results. • Provided real-time data.	• Minimum sample volume is usually required to perform tests. • Some analyses are subject to interference by other chemicals. • Target analytes must be known in order to be tested for.
Field Gas Chromatograph (GC)	Used for constituent-specific analysis of soil, soil vapor, and ground water samples for volatile and semi-volatile hydrocarbons. Consists of a column and detector (PID or FID).	• Definitive compound identification is possible. • Provides the highest data quality of all commonly used field analytical methods. Comparable to fixed-based laboratory results. • Low detection limits (approximately 0.08 mg/L for water). • Portable GCs may be carried into the field; transportable GCs are mounted to a mobile lab or direct push platform.	• Moderate to significant training is required to operate a field GC. • Extraction efficiency in clays and organic-rich soils may be lower than in other soil types. • Operating temperature range is generally between 40^o and 104^o F. • Certain chemicals may cause interference (e.g., alkane) with BTEX or PAH). • Instrument purchase/rental costs may be expensive.
Immunoassay Test Kits	Kits use antibodies to identify and measure target constituents through the use of an antibody-antigen reaction.	• Minimal training required. • Available for a wide range of organic and inorganic target analytes (see USEPA, 2001c). • For fuels, well-suited for measuring lighter aromatic petroleum fractions. • Reasonable correlation with laboratory results has been observed. • Equipment is portable and no electricity is required.	• Do not perform well for heavy petroleum hydrocarbons such as motor oil or grease. • Must be used within each manufacturer's specified temperature range (generally between 40^o and 90^o F. • Organic and clay-rich soil may limit effectiveness of extraction. • Prior knowledge of target analytes and potential interferences is necessary to select the correct test kit.

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TABLE D.7
FIELD SCREENING TECHNIQUES FOR GROUND WATER (Concluded)

Field Screening Technique	Description	Advantages	Limitations/Concerns
Direct Push Techniques (DPT)	Direct push analytical systems can incorporate techniques such as LIF (see TABLE D.2) or the Hydrosparge® to analyze ground water in situ. The Hydrosparge® sampler is lowered through a direct-push ground-water sampler that has been advanced into the water table, where it sparges (purges) VOCs from the ground water using inert gas; the VOCs are carried to a direct sampling ion trap mass spectrometer (DSITMS) detector on the surface for analysis.	• Real-time or near real-time data to be generated in the field while sampling, without the many requirements associated with sample management • Generates minimal investigation-derived waste (IDW). • Rapid and detailed assessment at a lower overall cost than could be achieved with more traditional methods such as drill rigs and fixed-base laboratories. • LIF attachments can detect gasoline, diesel fuel, jet fuels, fuel oil, motor oil, grease, and coal tar in the subsurface. • The Hydrosparge® allows VOCs in ground water to be analyzed without retrieving the direct-push rods and handling or packaging samples • Data collected with the Hydrosparge® are semi-quantitative.	• Detection limits can be higher and precision and accuracy lower than with traditional analytical methods. • Because experienced operators are generally required; May not be possible to lease the systems, and many may be offered as contract services only. • Practical vertical sampling limits are about 100 feet.

Sources: USEPA 1995b, 2001c

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D.2.3.7 Sample Preparation and Handling

Proper sample preparation and handling are necessary to maintain sample integrity. Prior to mobilizing to the field, the analyses for each sample that is being collected should be specified, and arrangements should be made to have the correct type of bottles, preservatives, holding times, and filtering requirements available to field personnel at the time of sampling. Samples should be labeled, logged (including appropriate chain-of-custody documentation), and handled using the techniques described in the standard method for each analyte. Preservation of ground-water samples is method-specific, and may include measures to control pH with chemical preservatives, refrigerate samples, and/or shield samples from light (USEPA, 1995b).

D.3 QUALITY ASSURANCE/QUALITY CONTROL

QA/QC samples are analyzed in addition to field samples and serve to validate the variability and usability of environmental sample results. Field replicate, background, and rinsate blank samples are commonly-collected field QA/QC samples. Performance evaluation, matrix spikes, and matrix spike duplicates are common QA/QC samples used by the laboratory for additional data verification. QA/QC samples are collected for all matrices sampled. **Table D.8** describes each type of QA/QC sample and its general purpose.

TABLE D.8
QUALITY ASSURANCE/QUALITY CONTROL SAMPLES

Sample Type	Sample Description and General Purpose	
Field Replicate (also called field duplicate or split sample)	Description:	Field samples obtained from one location, divided into separate containers and treated as separate samples throughout the remaining sample handling and analytical processes.
	Purpose:	Assess error associated with sample heterogeneity, sample methodology, and analytical procedures.
Background	Description:	Collected upgradient of areas of contamination where there is little or no chance of migration of the contaminants of concern.
	Purpose:	Provide a basis for comparison of target analyte concentrations with samples collected in the area of concern.
Rinseate Blank	Description:	Obtained by running analyte-free water over decontaminated sampling equipment and analyzing the rinseate.
	Purpose:	Assess cross-contamination brought about by improper decontamination procedures.
Performance Evaluation (PE)	Description:	Usually prepared by a third party, using a quantity of analyte that is unknown to the laboratory. The analyte used to prepare the PE sample is the same as the analyte of concern.
	Purpose:	Evaluate the overall bias of the analytical laboratory and detect any error in the analytical method used.

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TABLE D.8
QUALITY ASSURANCE/QUALITY CONTROL SAMPLES (Concluded)

Sample Type	Sample Description and General Purpose	
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	Description:	Environmental samples that are spiked in the laboratory with a known concentration of a target analyte to verify percent recoveries.
	Purpose:	Primarily used to check sample matrix interferences and/or to monitor laboratory or method performance.
Field Blank	Description:	Prepared in the field using certified clean water and are then submitted to the laboratory for analysis.
	Purpose:	Evaluate contamination error associated with sampling methodology and laboratory procedures.
Trip Blank	Description:	Prepared prior to going into the field; consist of certified clean water and are handled, transported, and analyzed in the same manner as the other volatile organic samples acquired that day.
	Purpose:	Evaluate error associated with sampling methodology and analytical procedures by determining if any contamination was introduced into samples during sampling, sample handling and shipment, and/or during laboratory handling and analysis.

Sources: USEPA, 1995a and 1995b.

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